

Partitioning of ^{129}I in the Environment:

The Fate of Radioiodine in a Shallow
Sand Aquifer System at Chalk River
Laboratories, Ontario, Canada

Report
To
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ABSTRACT

The transport behaviour and sorption characteristics of ^{127}I (stable iodine) and ^{129}I have been studied in a groundwater flow system at the Chalk River Laboratories, where sufficient quantities of both isotopes for measurement are present in soils, surface water, groundwater and vegetation due to infiltration from a low level waste management area into an underlying sandy aquifer. Stable iodine and ^{129}I concentrations in the recharge groundwater range up to $67\text{ }\mu\text{g/L}$ and $8.3 \times 10^{12}\text{ atoms/L}$, respectively.

Transfer factors required in dose assessment models, such as distribution coefficients (K_D) and concentration ratios (C_R) have been calculated from the data obtained. Differences observed between leachable and total concentrations of total I and ^{129}I indicate that ^{129}I does not have the same source as stable I.

A qualitative estimate of the inventories of ^{129}I in the various compartments existing along the flow path indicate that as much as 19% of the ^{129}I input may be sorbed on aquifer materials, and roughly 18% may be taken up by vegetation in the discharge area.

TABLE OF CONTENTS

1	INTRODUCTION	6
2	SETTING AND SOURCE	8
3	SAMPLING AND ANALYTICAL METHODS	9
3.1	Sampling	10
3.1.1	Sampling Groundwaters	10
3.1.2	Vegetation Sampling	11
3.1.3	Air Sampling	12
3.1.4	Core Collection and Storage	12
3.2	Analytical	13
3.2.1	Geochemistry of Groundwaters	13
3.2.2	Environmental Isotopes in Groundwater	13
3.2.3	Stable Iodine	14
3.2.4	Analysis of ^{129}I	14
3.3	Separation and Purification of Iodine Prior to Measurement	15
3.3.1	Separation of Iodide Bound to Different Fractions of the Soils	15
3.3.2	Combustion Technique	16
3.3.3	Separation and Purification of Iodine as AgI	16
3.3.4	Ion Chromatographic Separation of Brines	17
4	RESULTS and DISCUSSION	17
4.1	Geochemical Parameters	17
4.2	Systematics of ^{127}I and ^{129}I along the Flow Path	20
4.2.1	Iodine Measurements	20
4.2.2	Iodine in Recharge Area Groundwaters	20
4.2.3	Iodine in Discharge and Intermediate Area Groundwaters	21
4.2.4	Iodine and Chemical Variations along the Flow Path	22
4.3	Iodine Distribution Coefficients – K_d and C_R	24
4.3.1	Soil/Water K_D	24
4.3.2	Vegetation C_{RS}	25
4.3.3	Empirical Estimates of ^{129}I Mass Balance, and Comparison with Parameters Currently Used in Modelling	27
5	SUMMARY AND CONCLUSIONS	28
5.1	Geochemistry	28
5.2	Iodine	29
6	RECOMMENDATIONS FOR ADDITIONAL WORK	30
7	REFERENCES	32

TABLES

FIGURES

APPENDIX - Annotated Bibliography

LIST OF FIGURES

Figure 1 Geographic location of the Chalk River laboratories (CRL) and the position of Waste Management Area "C"

Figure 2 Stratigraphic section of flow system under study, oriented parallel to the groundwater flow

Figure 3 Piezometric grid in the vicinity of Area "C"

Figure 4 Spatial Distribution of stable I and ^{129}I in groundwaters sampled

Figure 5 Changes in stable I and ^{129}I down-gradient from the recharge zone beneath Area "C"

Figure 6 Changes in a) ^{129}I and b) stable I with increasing distance from Area "C"

Figure 7 Correlations between I, ^{129}I , other radioisotopes and chemical species present in all groundwaters sampled

Figure 8 Correlations between I, ^{129}I , other radioisotopes and chemical species in contaminant plume waters only

Figure 9 Plots of I versus ^{129}I both in and out of the plume

Figure 10 Empirical mass balance for ^{129}I along the flow path from Area "C" to Duke Swamp

LIST OF TABLES

Table 1. Stable iodine concentrations reported for a variety of terrestrial materials

Table 2. Methods in use for measurements of trace quantities of stable iodine

Table 3. Concentrations of ^{129}I and $^{129}\text{I}/\text{I}$ ratios reported for a variety of waters; precipitation, surface waters, groundwaters, brines.

Table 4. Selected soil/water K_D values for iodine in the published literature

Table 5a. Groundwater geochemical measurements

Table 5b. DOC, DIC, environmental isotope data and selected ion ratios measured

Table 6. Iodine and ^{129}I measurements in groundwater samples

Table 7. I and ^{129}I measurements in soils and soil leachates

Table 8. Summary of I and ^{129}I concentrations measured in soils and co-existing groundwaters, and calculated K_{ds}

Table 9. Summary of I and ^{129}I concentrations measured in vegetation and air samples collected at Duke Swamp, and calculated C_{RS}

1 INTRODUCTION

Iodine is an essential nutrient for most animals, including humans. It is found in trace concentrations in fresh and saline waters and in mineral and biological materials (Table 1). As a result, iodine cycling in the biosphere has been the subject of a large number of studies. Excellent review articles are available (e.g. Coughtrey et al., 1983; Whitehead, 1984; Fuge and Johnson, 1986). As part of this study, a literature review of previous work on iodine measurement and behaviour, including its transfer coefficients, has been carried out, and tables of relevant data (Tables 1 - 4) and a bibliography are attached as an Appendix to this report.

To date, a large number of laboratory studies (e.g. Behrens, 1982; Lieser and Steinkopff, 1989; Sheppard and Thibeault, 1990)) have addressed the measurement of potential adsorption-desorption of I from a variety of soils, and under a variety of conditions. However, there have been very few, if any, long-term, empirical field studies, chiefly because analytical techniques for the measurement of stable iodine at levels below 1 ppb have been extremely difficult.

In addition to the stable isotope, ^{127}I , twenty-three isotopes of iodine have been identified. One isotope, ^{129}I , has a natural origin in the upper atmosphere, through the interaction of high energy cosmic rays with xenon. It is also produced in the earth's crust, as a result of spontaneous and neutron-induced fission of heavy isotopes, mainly ^{238}U (Fabryka-Martin et al. 1985, Fabryka-Martin and Davis, 1987). Anthropogenic sources also contribute to global inventories of radioiodine. Atmospheric testing of nuclear weapons in the 1950s and 1960s dispersed large quantities of these and other fission products world-wide. Subsequent additions of radioiodine isotopes to the biosphere have resulted from their use as a diagnostic medical tool, from reactor operations, fuel re-processing (e.g. Beaujean et al., 1973), and, to a smaller extent, from the reactor accident at Chernobyl (Handl et al. 1993). Table 3 presents the ranges of concentration of ^{129}I in natural and anthropogenically-affected environments.

Considerable effort has been devoted to comparing the behaviour of radioiodine species with that of stable iodine, in order to gain an understanding of their cycling in both the short and long term.

Because of its very long half-life (15.7 million years), ^{129}I is potentially an important tool to monitor for the presence of nuclear facilities (e.g. Brauer and Ballou, 1975) and a source of radiological dose to the thyroid gland (e.g. NCRP Report No 75, 1983). It is of particular concern in the disposal of nuclear waste. Whether these wastes are incinerated or buried below the ground surface, physico-chemical mechanisms exist for ^{129}I to be re-deposited on the earth's surface, or to be transported by groundwater. While studies on the long-term effects of nuclear fuel waste management identify ^{129}I as a radionuclide of concern, Canadian and international studies modelling post-closure safety for disposal have had to rely on conservative assumptions and probabilistic estimates of environmental transport parameters to determine the long-term effects of ^{129}I . Detailed information regarding these parameters has been lacking because analytical techniques for the identification of low levels of ^{129}I were not available. These problems have been largely overcome by the development of accelerator mass spectrometry. A variety of new techniques for measurement of trace amounts of stable isotopes have also become available, in particular, inductively coupled plasma - mass spectrometry (ICP-MS). These developments should now allow measurements of in-situ sorption of ^{129}I and stable ^{127}I .

The objective of this study was to examine the transport behaviour and sorption characteristics of ^{129}I and I in a natural hydrogeological flow system where a source term well above current detection limits is available, and to then calculate the transfer factors required for dose assessment models. The scope of the study included groundwater and co-existing soil core analyses in regions of aquifer recharge and discharge, and groundwater analyses at several sites intermediate in the flow system, as well as a few air and vegetation measurements at the discharge site.

The aquifer studied follows a transect running from below a waste management area to a discharge site in a wetland approximately 300 m away. Cedar trees, growing at this site, or introduced into the wetland in an earlier experiment, either as potted or planted specimens, were used to study the uptake of ^{129}I by vegetation. To accomplish our objective a field and analytical program was undertaken that included the measurement of geochemical parameters, including major and trace elements, as well as stable I and ^{129}I . Any correlations observed between iodine and other elements might provide insight into the primary source(s) of the iodine. Since a number of the publications surveyed had indicated a strong correlation between iodine and carbon content

in both water and soils, dissolved organic and inorganic carbon, stable carbon ($^{13}\text{C}/^{12}\text{C}$) and ^{14}C analyses were also performed. ^3H measurements were done to provide a measure of conservative behaviour in this drainage system, and to allow the identification of changes that may have taken place since earlier studies were performed at the site (Killey et al. 1993). Transfer factors required in dose assessment models, such as the distribution coefficient (K_D), and the concentration ratio (C_R) have been calculated from the data collected.

2 SETTING AND SOURCE

This study has made use of a low level waste management site at the Chalk River laboratories (CRL) of Atomic Energy of Canada Limited, where anthropogenic ^{129}I is present in soils, surface waters, groundwaters, and vegetation in sufficient amounts to permit its measurement, and to allow the estimation of partitioning between the various compartments. The area has been well characterized hydrologically in a number of earlier studies, and detailed information on the release of $^{14}\text{CO}_2$ and HTO vapour at the discharge site, and their uptake by local vegetation, is available (Killey et al. 1993; Evenden et al. 1998; Milton et al. 1998)

The location and general hydrogeology of the site of these field studies has been described in some detail by Killey et al., (1993). Figure 1 is a map indicating the geographic location of the Chalk River Laboratories (CRL), and the position of Waste Management Area "C" (Area C) within it. Low level radioactive waste has been buried above the water table in this upland sand dune area since 1963. Infiltrating rain and snowmelt transport soluble components to the underlying aquifer. Figure 2 is a stratigraphic section oriented parallel to the groundwater flow. The aquifer is dominantly composed of fine to medium grain fluvial sand deposited during a high stage in glacial melt runoff along the Ottawa valley. These unconsolidated sands lie on crystalline bedrock. The upper aquifer was reworked into sand dunes during the early Holocene. The depth to the water table in the upper area exceeds 10 m. A laterally extensive unit of interstratified very fine to fine sands and sandy silts, as well as a thin unit of laminated clayey silts, exert considerable control over the regional hydrology. Discharge occurs about 300 m southwest of the Area C site,

in Duke Swamp. This area is comprised of 2.5 m of peaty organics underlain by unconsolidated sands.

The total annual precipitation at this site is approximately 800 mm, of which 37 % is available for recharge or runoff. In the dune deposits there is essentially no runoff, almost all available precipitation recharges the underlying unconfined aquifers. The average transit time for groundwaters moving from Area C to Duke Swamp has been estimated at 3 to 5 years using $^3\text{H}/^3\text{He}$ dating techniques on immediately adjacent areas (Noack, 1995). Figure 3 provides details of the piezometric grid installed in the study area.

Although waste suppliers are asked to provide clear identification of radionuclide contents, and wastes are screened prior to storage, there are no reliable records on the total ^{129}I buried at this site. This is not surprising, since identification of trace amounts of low energy beta emitters with very long half-lives has been exceedingly difficult. However, its presence in the waters discharging at Duke Swamp had been verified during scoping studies at that location in 1997 (Milton, private communication).

3 SAMPLING AND ANALYTICAL METHODS

A field program involving the sampling of groundwaters, soils, vegetation and air from the region between the Area C compound and Duke Swamp was undertaken in the autumn of 1997. Sampling activities were restricted to a transect from the uncovered portion of Area C (northern section) southwest to Duke Swamp. Groundwaters were sampled from three piezometer nests in the up-gradient region (C14, C111, C114), from two along the flow path (C8, C23), and from four nests in the discharge area and along the boundary with Duke Swamp (C213, C221, C210, C35). Soil samples were cored from sites adjacent to Area C (C114), and from Duke Swamp (C210). Vegetation samples were collected at an earlier date from potted and planted cedars in Duke Swamp and had been dried prior to storage. Details on the sampling and analytical program are presented here.

3.1 Sampling

3.1.1 Sampling Groundwaters

Groundwater samples were taken with a peristaltic pump from existing 5 cm diameter PVC piezometers installed during previous Area C studies. All piezometers were pumped to remove silts and very fine sands from tube screens and the formation surrounding the screen and to replace the standing column of groundwater within the piezometer with fresh groundwater. Before sample collection the piezometers were either pumped to remove at least 3 standing volumes of water or pumped until refusal. The piezometers were subsequently allowed to recharge before sampling. For piezometer nests with 5 cm diameter PVC standpipes installed to specific depths (C14, C114, C23, C8 and C35), a 3.2 cm diameter PVC tube was lowered to near the bottom of the piezometer, and water was pumped to surface. In the case of multi-level piezometers (C221 and C213) comprised of 0.625 cm diameter polyethylene tubes, the suction line was attached directly to the small diameter piezometer tube.

Groundwater samples were pressure filtered through a 0.45 μm membrane filters positioned downstream of the suction pump, collected in HDPE bottles (100-1000ml), and stored at 4°C until analysis. Alkalinity analyses of all samples were conducted on site, using HACH Digital titration (Model 16900-01). Separate sample bottles were collected for anion, cation, and isotope (^{13}C , ^{14}C , ^3H) analyses. Samples collected for DOC and cation analysis (50 ml) were acidified to pH 2 with 10% (v/v) HCl.

One litre samples were collected for I and ^{129}I analyses. A 20 mL sample was removed from each and sent to the General Chemistry Branch at CRL for stable iodide measurements by ICP-MS. Dilute NaOH was added to the remaining sample to raise the pH to 10 prior to storage at 4°C. When substantial differences were noted between the October/97 values and those obtained in earlier scoping studies (May/97) for both iodine isotopes at boreholes in the recharge and discharge zones (C114 and C210), repeat samplings at C114 and C210 were performed in July 1998 in order to ascertain whether such variations in the concentrations of radioactive species were seasonal.

Because of the large differences between the spring and fall sampling periods for both ^{129}I and ^3H (approximately 10 fold), it was decided that the weighted average values would be used for K_D calculations, but only the 97 October measurements from all the piezometers would be intercompared along the flowpath. A complete re-sampling was beyond the financial and time limitations of the study.

3.1.2 *Vegetation Sampling*

Undertaking a detailed vegetation study was outside the limitations of this study. However, a previous experiment had been performed at the Duke Swamp site in 1997 to examine the relative importance of atmospheric and root uptake of ^3H and ^{14}C in small cedar trees translocated to this discharge zone for an 8 week period (Kotzer and Milton, private communication). Two plants were left in their pots, which were placed in plastic trays to avoid any moisture uptake from the native soil. Two other plants were removed from their pots, and planted in the swampy soil. During this exposure, fresh growth needles were picked weekly from all 4 plants using plastic gloves during all aspects of sample handling. A fifth plant remained off site (Deep River), and was used to establish background concentrations of the radioisotopes under study. Lichen samples collected from nearby trees, at approximately the same height from the ground as the cedar sampling was done, were used to provide information on the equilibrium air concentrations.

Very fortunately, samples remaining following the completion of this experiment could be made available for the present study. Only those samples collected at the beginning and end of the 8 week period were processed for this study, since our primary aim was to establish whether iodide uptake over short periods would be measurable. In addition a sample of fresh growth from a large cedar tree growing in the swamp was also collected during 1997, as a means of establishing the existence of a gradient in ^{129}I air concentration with height above ground. Trace concentrations taken up by needles and leaves are very rapidly mixed throughout the plant; hence taller trees would show lower average concentrations if such a gradient exists.

3.1.3 Air Sampling

Air samples were collected by bubbling air through NaOH solutions at approximately 0.5L per minute, in one case for 8 hours, and another for 3 days. It was hoped that these samples would provide us with the means to evaluate atmospheric ^{129}I and ^{127}I available for uptake by the plants; unfortunately neither sampling period collected enough stable iodide to permit its measurement. It appears that several cubic metres of air would be required to provide a measurable quantity of stable iodine species.

3.1.4 Core Collection and Storage

Two cores of sediments from the study area were collected, namely (1) a core of the sands near the recharge area (C-114, immediately above and within the contaminant plume) and (2) a core of peats that have accumulated over several thousand years, plus the underlying sands, in the Duke Swamp (C-210). Samples from specific depths (C114 - 4.6 to 10m., and C210 - 0 to 4.6m.) were chosen primarily on the basis of stratigraphic boundaries (Killey et al., 1993). The cores in the recharge area were extracted using 9.5 cm ID hollow stem augers, driven by a CME-75 rotary rig, collecting continuous cores of sediment ahead of the augers using a 5 cm by 0.5-1.0 m long piston corer (Killey et al., 1993). Due to restricted access in Duke Swamp, a portable, gasoline-powered jackhammer was used to drive the piston sampler and core barrel. Organic soils were sampled by driving a 3 m long 5.0 cm ID aluminum tube core barrel into the organic soil until increased resistance to penetration was observed indicating intersection with the underlying silty sands or sands. In order to avoid contamination, the core samples were stored at 4° C in the aluminum tubes. Subsequently, they were cut open lengthwise. The sediment was removed and dried at 80° C for 24 hours, ground with a mortar and pestle, homogenized and stored until leaching and/or pyrolytic extraction.

In order to determine ^{127}I and ^{129}I levels in nearby sands containing very low levels of ^3H and ^{14}C , grab samples of surface sand at different depths on an exposed aeolian sand dune face were also collected at a site outside the contaminated zone (Twin Lakes area). These samples were dried at 80° C for 24 hours and processed in a similar manner. Unfortunately, no water samples were available from this area, therefore data from this site has not been included in the discussion.

3.2 Analytical

3.2.1 Geochemistry of Groundwaters

Major element analyses were undertaken at the Geochemistry Laboratory, Department of Earth Sciences, University of Ottawa. Cations were analyzed with a Perkin-Elmer ICP-AES and anions were measured with a Dionex DX-100 ion chromatograph. DOC analysis was performed on an Astro 2001 total organic carbon autoanalyzer.

Geochemical data were treated with the geochemical code WATEQ4F (Ball, 1991) to determine mineral saturation indices. These are given for relevant minerals in Table 5.

3.2.2 Environmental Isotopes in Groundwater

Carbon-13 was measured in the G.G. Hatch Isotope Laboratories on CO₂ generated by the reaction of 85% phosphoric acid with the water sample and analyzed on an automated triple collector VG SIRA 12 gas source mass spectrometer (precision of 0.10‰). Isotopic results are expressed in standard δ-‰ fashion against VPDB, according to:

$$\delta^{13}\text{C}_{\text{sample}} = \left(\frac{R_{\text{sample}}}{R_{\text{VPDB}}} - 1 \right) \cdot 10^3 \text{ ‰ VPDB} \quad \text{where } R = \frac{^{13}\text{C}}{^{12}\text{C}}$$

Carbon-14 activity in water samples was measured by direct counting of β⁻ decay events at the ¹⁴C energy level in an 18 ml cocktail of water sample and scintillation agent. ¹⁴C activities (Bq/ml) and specific activities (Bq¹⁴C per gram dissolved carbon) are listed in Table 5b. Tritium was similarly measured by direct counting of water/scintillator mixtures (Table 5b). These radioactivity measurements were performed in the Environmental Research Branch, CRL using a Packard 1550 Liquid Scintillation Counter. Lower limits of detection for this method are 0.01 Bq/ml for ³H and 0.03 Bq/ml carbon for ¹⁴C.

3.2.3 Stable Iodine

The concentration of I in natural settings is highly variable (Table 1). The major chemical form in fresh water environments is thought to be I^- (Paquette et al., 1986). Consequently the terms iodide and stable I have been used interchangeably in this report. A variety of analytical methods permit measurement to less than 1 $\mu\text{g/L}$ (Table 2). Stephenson and Motycka (1994) have reviewed these methods in detail, and the reader is referred to that paper for more information. For this study, inductively coupled plasma – mass spectrometry was used. The good linearity inherent in ICP-MS allows analysis of samples with highly variable I concentrations. Samples were run using the ICP-MS facility in the General Chemistry Branch of AECL at Chalk River. Unfortunately brines, coloured samples, and those with high NaOH concentrations are not suitable for measurement by this method. A colorimetric (spectrophotometric) method was substituted for the analysis of MgCl_2 leach solutions in this study.

3.2.4 Analysis of ^{129}I

Methods employed for analysis of ^{129}I in natural samples include counting β^- decay, neutron activation analysis (NAA) and accelerator mass spectrometry (AMS) (McHugh and Sheffield 1965; Brauer and Kaye 1974). Table 3 indicates the concentrations of ^{129}I and $^{129}\text{I}/\text{I}$ ratios measured for various waters. Due to the long half-life of ^{129}I , determination by β^- decay is useful only for large samples with very high activities. Determination of ^{129}I by neutron activation analysis of ^{130}I as a result of the reaction $^{129}\text{I}(n,\chi)^{130}\text{I}$ is suitable for determining quantities of ^{129}I on the order of 10^{10} to 10^{12} atoms. Neutron activation analysis, although it has been quite successful (Muramatsu and Ohmomo 1986) has sensitivity limitations, due to production of extraneous ^{129}I from trace impurities in samples (Elmore et al. 1980). Measurements of ^{129}I using a three-stage mass spectrometer and negative ion sputter source resulted in sensitivities of approximately 10^9 atoms, although the method is subject to isobaric interferences near mass 129 from species such as $^{97}\text{MoO}_2^-$ (McHugh and Sheffield 1965). More recently, measurement of ^{129}I by negative ionization mass spectrometry has resulted in radically improved atomic sensitivities (10^7 atoms), although $^{129}\text{I}/\text{I}$ ratio sensitivities are still limited to approximately 10^{-8} (Delmore 1982; Stouffels 1982).

Currently, the most widely applied method for determining low-level environmental ^{129}I concentrations and $^{129}\text{I}/\text{I}$ ratios is accelerator mass spectrometry, which requires only approximately 2 to 10 mg of iodine for preparation of a suitable target (Elmore et al. 1980; Cornett et al., 1997; Koslowsky et al., 1997). The method employed is similar to that used for ^{36}Cl measurements (Elmore et al. 1979), except a time-of-flight detector is used for the final determination of ^{129}I . Using the AMS method, Elmore et al. (1980) found only one isobaric interference with ^{129}I , ^{129}Xe , whose effects were substantial at very low ^{129}I concentrations only (one atom of $^{129}\text{I}/10^{18}$ atoms of stable ^{127}I). Elmore et al. (1980) and Fabryka-Martin et al. (1985) indicated that the sensitivity of the accelerator method was approximately 10^7 atoms ^{129}I , or $^{129}\text{I}/\text{I}$ ratios on the order of 10^{-13} . Similar measurement capabilities have been demonstrated in several other studies for ^{129}I in groundwater and hydrocarbon samples (e.g., Fehn et al. 1986, 1987, 1990, 1992; Kotzer et al., 1999).

3.3 Separation and Purification of Iodine Prior to Measurement

3.3.1 *Separation of Iodide Bound to Different Fractions of the Soils*

Samples of the cores obtained at C114 and C210, as well as Twin Lake dune samples were sequentially leached to obtain information on the in-situ iodine. An abbreviated version of the method of Tessier et al. (1979) was used to extract iodine from three different phases: i) exchangeable iodide, ii) iodide bound to iron and manganese oxyhydroxides, and iii) iodine species bound to organic matter. The method used is as follows:

i) exchangeable – 20 g of sediment were shaken with 200 ml of 1M MgCl_2 for 1 hour and centrifuged. (It is assumed that this fraction will also contain the water-soluble components)

ii) oxyhydroxide-bound – the separated solid from i) was next shaken with 200 ml of 0.04M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (hydroxylamine hydrochloride) in 25%(v/v) HOAc (acetic acid) for 8 hours at 96°C , then centrifuged.

iii) organically bound – the separated solid in ii) was shaken with 6N HNO_3 . However, the solution rapidly became very dark in colour, rendering it impossible to prepare a clean target or carry out a stable iodide measurement. Consequently a second sub-sample of each of the sediments tested was soaked in 1M KOH for 24 hours. In the case of the sandy sediments, 50 ml of KOH was added to 40 g of sample. For the peat, 100 ml of KOH was added to 20 g of organic sediments. The resulting solutions were relatively clear, and the samples were prepared for AMS; unfortunately the concentration of OH^- was considerably too high for ICP-MS injection..

3.3.2 Combustion Technique

Total iodine was recovered from soil and vegetation samples by pyrolysis. The technique utilizes a quartz tube furnace in which a wet oxygen stream is allowed to flow over a nickel boat containing the sample (sample size 0.5 g of vegetation; 1-2 g soil, plus .03 g V_2O_5 accelerator). The combustion gases are bubbled into a receptor containing dilute NaOH. Details of the method are documented in Chant et al. (1996).

Because of analytical difficulties for stable I using the ICP-MS when high concentrations of OH^- are present, the combusted gases were bubbled into a receptor containing distilled water only. In order to check the recoveries of iodide under these conditions, a radio-tracer was used. A known amount of ^{125}I was added to the sample, and allowed to equilibrate before combustion. The amount of ^{125}I in the combustion receptor solution was measured and used to determine an efficiency factor for collection of I and ^{129}I in the combustion procedure (this method has been tested successfully on secondary standards.). The measured I and ^{129}I were subsequently corrected on the basis of the ^{125}I results.

3.3.3 Separation and Purification of Iodine as AgI

Iodine was recovered from both water samples and from receptor solutions used in solid sample treatment, in the form of AgI . Following removal of a known volume of the solution for stable iodide determination by ICP/MS, a known quantity of iodide (usually 10 mg) was added as a

carrier, in order to have sufficient stable iodide to provide a suitable target for AMS. The solution was shaken to permit complete exchange of iodine species, the pH was adjusted to 2 with HNO_3 and sufficient AgNO_3 was added to precipitate all the I^- and Cl^- present. The precipitate was allowed to settle in the dark, then decanted. The recovered AgI/AgCl precipitate was rinsed with double-distilled (d.d.) H_2O and treated with NH_4OH to remove any AgCl . The remaining AgI was subsequently washed 3 times with d.d. H_2O , 3 times with methanol, and dried prior to shipment to Isotrace Laboratory, University of Toronto, for measurement of ^{129}I .

Blanks prepared by adding 10 mg of I^- carrier solution to the usual sample volume of water or leach solution were processed by the above procedure, and sent for AMS measurement also, to provide a measure of the ^{129}I activity introduced during sample preparation (i.e. procedural background).

3.3.4 Ion Chromatographic Separation of Brines

Samples containing very high concentrations of chloride required the insertion of a Cl-I separation step prior to precipitation with AgNO_3 . The procedure, which is described in detail in Ross and Gascoyne (1995), consisted of addition of carrier I^- , adsorption of iodide on Dowex 1 anion resin in sulfate form, elution in HOCl , oxidation to I_2 , extraction into CCl_4 , reduction and back-extraction into dilute sodium bisulfite.

4 RESULTS and DISCUSSION

4.1 Geochemical Parameters

The results of the geochemical analyses of groundwater samples are given in Tables 5a,b. The groundwaters throughout the flow system are characterized by Na-Ca/Cl-HCO_3 geochemical facies (Table 5a). No strong distinction is apparent between groundwaters in the recharge area with the exception of a higher Na-Cl component in the samples from C14. Recharge area groundwaters generally have between 55 and 90 mg/L Cl^- , but are as high as 672 mg/L (C14-7).

In some cases the strong Cl^- geochemical component in some groundwaters is fully supported by Na^+ , indicating a NaCl source (the upper portion of the aquifer is recharged by Lake 233, which is known to be contaminated with road salt). Most samples have a Cl^- excess relative to Na^+ , which may be due to cation exchange within the aquifer. Only two samples have a strong Na^+ excess, indicating additional sources of Na^+ .

The boundaries of the contaminant plume from Area C is functionally defined here by tritium activities greater than 10 Bq/ml (Figure 3). Cross-correlation of ^3H with other geochemical species provides no statistical evidence that any dissolved geochemical species other than ^{14}C is derived from the waste compound. Killey et al. (1993) describe the water quality of the contaminant plume from Area C as a dilute landfill leachate. However, sites with very low to no measurable tritium (e.g. C35) show no distinction for major and minor trace elements from that of high tritium samples, other than low ^{14}C .

Groundwaters along the flow path from Area C to the discharge zone near Duke Swamp show little variation in pH, and are consistently less than neutral, averaging 5.7. This acidity can be attributed to dissolution of CO_2 , with perhaps a minor contribution from humic and fulvic acids.

The concentration of Ca^{2+} in all groundwaters (6.6 to 43.4 mg/L) reflects the low reactivity of the quartz sand aquifer. Minor contributions of Ca^{2+} may come from weathering of feldspar grains within the aquifer, or release from clay minerals through cation exchange for Na^+ . Treatment of the data with the WATEQ4 geochemical code indicates that calcite is highly undersaturated ($\log \text{SI}_{\text{cal}} = -3.3$ to -3.5 , where $\log \text{SI} = \log (\text{ion activity product/mineral solubility constant})$ (Table 5a). Similarly, silicate alteration products, including kaolinite and illite, are highly undersaturated. These waters are, however, close to saturation with respect to amorphous silica. Clearly, the relatively short subsurface flow path and relatively unreactive quartz sand aquifer preclude extensive weathering reactions and consumption of CO_2 acidity.

All groundwaters have elevated DOC, with values varying between a minimum of 8 mg-C/L to a maximum of 26 mg-C/L, representing between 14 and 75% of the total dissolved carbon. The source of this organic carbon is not known, and may be a combination of organic waste from

Area C, ^{14}C -active organics leached from soils in the vicinity of Area C, and sedimentary organic material within the late Quaternary sands. Killey et al (1993) show that up to 10% of the ^{14}C -activity in the contaminant plume is carried by DOC. Given the high ^{14}C -activity of the dissolved carbon (DIC plus DOC), which varies between 10 and 75 Bq/g, much of this carbon must be derived from recharge through and adjacent to Area C.

Groundwater Eh was not measured directly. However, nitrate, sulphate and dissolved iron provide a relative indication of aquifer redox conditions. Dissolved iron concentrations vary from less than 1 mg/L to over 50 mg/L. For the range in pH values in these groundwaters, Fe concentrations greater than 1 mg/L are attributed to the reduced Fe^{2+} species. Thus, samples with elevated Fe concentration represent low redox potential. Inverse correlations with electron acceptors including NO_3^- and SO_4^{2-} corroborates this observation. With the exception of C213-4, which is affected by surface water infiltration, groundwaters with Fe concentrations greater than 1 mg/L have no detectable nitrate, while those with low Fe have measurable NO_3^- (up to 38 mg/L). A similar inverse correlation is observed for SO_4^{2-} . There is no consistent pattern for the distribution of Fe. Elevated concentrations are observed in samples from the recharge area and from the discharge area near Duke Swamp. However, low Fe concentrations (oxidizing conditions) are similarly observed in both regions. Neither is there an indication that reducing conditions correlate with increased depth or DOC. A possible interpretation is that oxidizing (low Fe) conditions occur in areas of greater permeability where dissolved O_2 transport from the recharge area is greater.

The low pH values are accompanied by high CO_2 partial pressures throughout the flow system. Log P_{CO_2} in recharge area varies between -1.29 and -2.38 with a geometric mean of -1.7. This is common for soil P_{CO_2} values, which typically vary between -1.5 and -2.5. Values for samples from the discharge area vary between -0.02 and -2.29 with a geometric mean of -0.8. Intermediate samples (C8 and C23) have a geometric mean of -1.3 for log P_{CO_2} . The increased P_{CO_2} of the down-gradient samples clearly indicates a subsurface source of CO_2 , generated under closed system conditions in the saturated zone of the aquifer. The high dissolved organic carbon found in most samples is a likely source of CO_2 , through aerobic and anaerobic oxidation, as is

the oxidation of solid organic carbon (peat) in the discharge zone. This is consistent with the ^{13}C content measured for dissolved inorganic carbon ($\delta^{13}\text{C}_{\text{DIC}}$), which averages -20.6‰ for the up-gradient piezometers and -19.8‰ for the down-gradient sites (Table 5b). These values are close to the $\delta^{13}\text{C}$ value of -23‰ , which is typical of soil CO_2 in temperate landscapes. Duke swamp runoff has geochemical characteristics similar to those of groundwaters in the discharge area. However, equilibration with the atmosphere is probably responsible for the slightly elevated pH, lower DIC and decreased P_{CO_2} .

Modelling of the pH - $\delta^{13}\text{C}$ conditions for recharge of these groundwaters in high P_{CO_2} soils shows that the $\delta^{13}\text{C}$ for groundwater DIC are consistent with uptake of microbially respired CO_2 with minimal dissolution of carbonate minerals. This is consistent with the highly undersaturated conditions for calcite in these waters (Table 5b), and low pH values.

4.2 Systematics of ^{127}I and ^{129}I along the Flow Path

4.2.1 Iodine Measurements

The measurements of total iodine and ^{129}I are given in Table 6. Analytical results for soils, selective leaches from soil samples, vegetation and air samples are given in Tables 7 and 8. Overall, stable iodine and $^{129}\text{I}/\text{I}$ ratios measured for the sampled piezometers varied from 0.23 to 67 ppb and 2.1×10^{-13} to 4.8×10^{-9} respectively (not dilution-corrected). The latter values translate to 1.0×10^8 to 8.3×10^{11} atoms $^{129}\text{I}/\text{L}$ (Table 6).

4.2.2 Iodine in Recharge Area Groundwaters

Groundwaters from piezometers nearest to Area C recharge (C14, C111, C114) have uncorrected $^{129}\text{I}/\text{I}$ ratios between 1.9×10^{-12} to 4.8×10^{-9} and ^{129}I concentrations of 8.9×10^8 to 8.3×10^{11} atoms/L, respectively (Figure 4, Table 6). At borehole C-114, groundwaters from the contaminant plume (8 m depth) were sampled at several different time periods throughout the study and found to contain I and ^{129}I levels between 6.9 to 67 ppb and 6.0×10^{10} to 8.3×10^{11} a/L, respectively (Table 6). The lowest concentrations of I and ^{129}I occurred in October 1997, but

were as much as an order of magnitude higher in both I and ^{129}I in May 1997 and July 1998. Tritium levels in the October 1997 and June 1998 water samples show a similar variation (Table 5b).

Long-term records of the water-table levels in the recharge area suggest that the position of the water table varies by as much as 1.5 m annually with the highest water levels in early summer and decreasing levels throughout the rest of the year. The maximum contaminant plume concentrations occur over a very limited depth interval (~0.5 to 1 m) which coincides with the water table. Displacement of the water table relative to the screened section of the piezometer later in the year may then result in substantial changes in the observed concentrations in the contaminant plume. Although the seasonal I and ^{129}I differences are substantial (approximately 4 to 15x), the resultant effect over the entire length of the sand aquifer may be minimized because of the high hydraulic conductivities (10^{-2} to 10^{-3} cm/s) and relatively fast groundwater-flow velocities (~0.25 m/day - Noack, 1995). Consequently, the measurements of all three sampling dates at C114-8 have been averaged, resulting in concentrations of 40.1 ppb I and 5.5×10^{11} a/L ^{129}I . The two other piezometers sampled near the recharge area on October 1997 (C14, C111) have lower concentrations of I and ^{129}I . This suggests that either the source for I and ^{129}I in Area C is quite heterogeneous or these piezometers may have been similarly affected by the differences in sampling times and associated water table levels. Concentrations of ^{129}I (9.8×10^8 to 8.28×10^{11} atoms/L - Table 6) within the contaminant plume are generally higher (~10x) than adjacent samples taken from above or below the plume (1.04×10^9 to 1.66×10^9 atoms/L - Table 6), which supports our hypothesis that ^{129}I , like tritium and ^{14}C , originates from Area C wastes.

4.2.3 Iodine in Discharge and Intermediate Area Groundwaters

Groundwaters from piezometers within or near the groundwater discharge area at Duke Swamp (C210, C-213, C-221) have stable I (0.23 to 26 ppb) and ^{129}I concentrations (1.0×10^8 to 8.4×10^{10} atoms $^{129}\text{I}/\text{L}$) which are slightly lower than the average for recharge-area groundwaters from borehole C-114 at a depth of 8 m. Waters from C210 were sampled in May 1997 and October 1997 and contained ^{129}I levels of 5.4×10^{10} and 8.4×10^{10} atoms/L, respectively (average value 6.9×10^{10}). This lesser degree of variability was to be expected at the end of the flow system. In

similar fashion to the recharge area, contaminant plume groundwaters had higher tritium, ^{14}C , I and ^{129}I levels relative to adjacent, out-of-plume groundwaters (Figure 4, Tables 5b,6). Groundwaters from locations between the recharge and discharge areas have stable I and ^{129}I concentrations which are between 1.5 and 13.0 ppb and 2.9×10^9 to 4.8×10^{10} atoms/L. These levels are similar to those measured in several of the piezometers at or near the discharge area in Duke Swamp.

4.2.4 Iodine and Chemical Variations along the Flow Path

Examination of the spatial distributions of I and ^{129}I in the groundwaters suggest that, in the direction of groundwater flow, there is a limited amount of change in their concentrations. If we consider that contaminant plume groundwaters from piezometers in boreholes C114 - C8 - C213 - C210 represent a single, continuous plume of elevated ^{129}I in the direction of groundwater flow, then there is a decrease in I and ^{129}I by a factor of between 1.5 and 8 between recharge and discharge (Figure 5). It is not entirely clear if all of the observed decrease in I and ^{129}I can be attributed to loss in the flow system, as part of the observed decrease can easily be accounted for in the observed degree of natural variation in ^{129}I concentrations lateral to flow. This suggests either a heterogeneous input function or that the internal stratigraphy of the sand aquifer is controlling the distribution of the radionuclides within the aquifer. Laterally- and horizontally-constrained distribution of ^{14}C and tritium within the aquifer near the discharge point, with the highest ^{14}C concentrations centered near C212 - C213 and highest tritium levels slightly more northwest (near C221- C222; Killey et al., 1998) suggests both these hypotheses may be reasonable. A similar scenario is observed for boreholes near the recharge site, with C14 and C111 depleted in ^{14}C , ^3H , and ^{129}I relative to C114. Concentrations of ^{129}I above natural background levels, even near the extreme edge of the contaminant plume (C-35), indicate it is being influenced by longitudinal and transverse dispersion processes resulting in a concentration gradient away from the center of the plume, similar to that observed for ^{14}C (Killey et al., 1998).

Along the length of the flow system, comparison of the concentrations of ^{129}I (Figure 6a) and stable I (Figure 6b) coincident with the contaminant plume and adjacent to the contaminant plume indicates that there is approximately an order of magnitude more I and ^{129}I in the contaminant

plume groundwaters. Tritium and ^{14}C show similar variations. This indicates that the I, and ^{129}I , in the aquifer is intrinsically associated with the physico-chemical processes responsible for the higher tritium and ^{14}C .

The systematics of I and ^{129}I have been compared with the concentrations of several species and nuclides in the groundwaters in an effort to identify the physico-chemical nature of the controls on the systematics of I in the subsurface. Tritium, I and ^{129}I concentrations in all groundwaters are relatively well-constrained, with correlation co-efficients between 0.58 and 0.87; ^{14}C is less correlated (Figure 7 a - d). The relationship between I - ^{129}I and dissolved organic carbon and total alkalinity in all groundwaters is much less well-defined, with correlation co-efficients of <0.1 to 0.20 (Figure 7 e - h). For waters sampled within the contaminant plume only, there is still a strong correlation between ^{129}I , I and tritium and, again, slightly less for ^{14}C (Figure 8 a-d). However, there is a much better correlation between ^{129}I , DOC and alkalinity for groundwaters from the contaminant plume (Figure 8 e-h) than for all the groundwater samples (Figure 7 e-h). The correlation between I and ^{129}I is shown graphically in Figure 9.

The source of carbonate alkalinity in the contaminant plume groundwaters is of mixed origin, including DIC originating from soils in the recharge area, a minor contribution from the aquifer matrix (carbonate minerals) and oxidation of dissolved organic constituents which have originated from the Area C wastes (D. Killey - personal communication). Killey et al. (1998) observed a better correlation between DIC - ^{14}C than DOC - ^{14}C . Based on the limited amount of data here, it is unclear whether or not the same relationship exists between DIC - iodine and DOC - iodine. The nature of species comprising both the alkalinity and DOC has not been determined in this study. This is recommended in any future work. Overall, there appears to be strong association between I (and ^{129}I) and tritium in the groundwaters. As HTO is largely considered to be conservative in a groundwater system with respect to water/rock interactions, this association may suggest that, for the sands in the Area C flow system, I is behaving conservatively.

4.3 Iodine Distribution Coefficients – K_d and C_R

Several sections of cored sediments and peats near C114 and C210 have been combusted using pyrolysis techniques and their concentrations of I and ^{129}I were measured (Table 7). Similar measurements have also been made on solutions resulting from sequential leachs of the cored materials. A comparison between the amounts of I and ^{129}I in, and adsorbed to, the solid matrix and the co-existing groundwaters has been made to provide an indication of the degree of retention of I and ^{129}I by the aquifer matrix, and to explain qualitatively the distribution of ^{129}I and I within the groundwaters. As outlined in the Introduction, a number of vegetative samples which had previously been exposed in Duke Swamp for a short period were also combusted, and the increases in concentrations of ^{129}I were measured in both potted and planted specimens.

4.3.1 Soil/Water K_D

The data reported in Tables 7 and 8 indicate that the bulk of the ^{129}I is loosely bound to solid coatings on the aquifer solids, and can be released by a hydroxylamine hydrochloride leach. Less than about 25% of the total leachable ^{129}I was present in a readily exchangeable form (i.e. leachable by MgCl_2). It is unfortunate that comparable data are not available for stable iodide, since the background values reported by ICP/MS for the hydroxylamine solution were high and extremely variable, rendering all but one of the concentrations totally untrustworthy. At least one half of the stable I measured in the combusted peat sample (210 A) was recovered in the NH_2OH leach, suggesting that in this case stable I may be present in both the surface coatings and the matrix materials. The fact that the total leachable ^{129}I exceeds the combustion values in three out of four samples probably results from a combination of heterogeneity of adsorbed oxides, hydroxides, etc. in this porous medium, differing sample sizes used (i.e. 20 g samples were leached, one g samples were combusted) and the sum of errors at all stages of these measurements, which are on the order of 10-15%.

The data in Table 4 cover a wide range of soils and experimental conditions. If we assume that a sediment to water ratio down to 1/10 exists in the sand aquifer under study, the values listed in the compilations of Sheppard and Thibeault (1990) are probably most applicable here. The mean

K_D listed for sand is 1, within a range of 0.04-81. Measured K_{Ds} for ^{129}I in three samples taken from sandy sediment cores inside and outside the plume (Table 8: 114-A, 114-C, 210-B) fit well inside these limits, and are internally consistent within a factor of 4 (5.5 - 21.4).

These low K_{Ds} suggest, as does the correlation between tritium, ^{129}I and I (Figures 4 and 5 a,b), that I may be behaving conservatively in the groundwaters migrating through the sands at Area C. Several factors may be involved: (1) rapid movement of the contaminant plume in the subsurface, possibly not allowing enough time for equilibrium adsorption to take place or, (2) large changes in the position of the water table between Spring and Fall resulting in large changes in iodine concentrations.

The mean K_D value for organic soils in Sheppard and Thibeault's 1990 compilation is 25 (range 1.4 - 368). The retention for stable I and ^{129}I calculated for the contaminant plume in the discharge zone (210-A), is in line with this range (Table 8, $K_{Ds} = 303$ and 273 respectively). The higher value, relative to those for the sands, may result from interaction with the very large microbial population to be expected in a zone of high organic content or interactions with substantial amounts of ferrous oxyhydroxides precipitating out of the groundwater towards the end of the flow path. It is also probable that some ^{129}I may have been returned to the soil surface in litter following its uptake in vegetation, as has the bulk of the ^{14}C present in these peats. A cold KOH leach designed to degrade the organic molecules released <10% of the total (combustion) ^{129}I ; unfortunately stable iodide analyses of the KOH leachates have proved too difficult by our current methods.

4.3.2 *Vegetation C_{RS}*

The few values available for ^{129}I concentrations in precipitation and surface water in Eastern Ontario are listed in Table 3. Since stable iodide concentrations were not measured in any of these samples, the ratios have either not been corrected for dilution, or the correction made is an estimate only (Krestow, 1996). Hence we prefer to place more confidence in the atoms/L values, which are in reasonable agreement with the limited number of values reported elsewhere

(Fabryka-Martin, 1985). Unfortunately, under these circumstances direct comparisons of precipitation data with measurements in air and vegetation are not possible.

There appears to be at least an order of magnitude difference in ^{129}I concentrations in precipitation near the CRL stack and outside the laboratory proper (Deep River) (Table 3). Other studies on dispersion of stack-released volatiles (^{14}C , Milton et al. 1995; ^{36}Cl , Milton et al. 1994) have indicated that a decrease in concentration of 2.5 to 10 times can be expected between the point of release and the Duke Swamp region, approximately 3.5 km distant. While it is probable that iodine will behave similarly to particle-reactive chlorine, we prefer, in this instance, to use the more conservative value for dispersion, leading to an estimate of $<9 \times 10^8$ atoms/L in precipitation at the discharge site. This value is not significantly different from that measured in the lichen sample collected at the plant exposure site. Thus, it is not possible at this time to check our hypothesis that appreciable ^{129}I is being released from discharging waters, or volatilizing from the soil surface, and in so doing contributing to the foliar uptake of this radionuclide in either the exposed potted plant or in the lichen.

On the basis of the data in Table 9, concentration ratios (C_R) have been calculated. It must be stressed that these are not equilibrium ratios, but are dynamic ratios resulting from an 8 week exposure. Amiro et al (1993) have calculated an empirical plant/soil concentration ratio. However, they note that in practice the C_R for I encompasses both the uptake from the soil by roots and deposition to foliage from the atmosphere. In our experiment we have attempted to separate these two influences. C_R (water) is defined as atoms ^{129}I per kg vegetation / atoms ^{129}I per litre of water. In this case we have used the difference between the values for planted and potted plants to represent the atoms ^{129}I contributed by the transpirational water per kg vegetation, subtracting the base, or off -site, original concentrations in both cases, resulting in a C_R of 3.0

C_R (air) is defined as atoms ^{129}I per kg vegetation / atoms ^{129}I per m^3 air. In this case we have used the value for the potted plant to represent the atoms of ^{129}I contributed by the atmosphere per kg vegetation, following subtraction of the original concentration of this radionuclide in the plant.

Our single determination for ^{129}I in air has a large associated error, since the sample size was very small, consequently this C_R (air) value of 3.7×10^{-3} should be considered an estimate only.

The data in Table 9 indicate that ^{129}I is taken up rapidly by plants, both from a mixed air and groundwater source, and from an atmospheric source only. The relative contribution of the two sources is approximately 10:1 (water: air), over this time period. However, the accumulation of iodine and other halides on the surfaces of spruce needles, and its correlation with ambient air concentrations and needle age, suggesting foliar uptake, has been well documented (Wytenbach et al., 1997). It is probable that over longer time scales, the contribution of foliar uptake, via the stomata, will surpass that of root uptake, via the transpirational stream. This finding is in line with the observed major influence of atmospheric uptake on the assimilation of ^{14}C and ^3H in plants (Kotzer and Milton, private communication). Additional ^{129}I measurements in air and precipitation, and longer plant exposure times, are required before we can quantify the contribution of volatilization from soils and discharging waters to the total atmospheric signal.

4.3.3 Empirical Estimates of ^{129}I Mass Balance, and Comparison with Parameters Currently Used in Modelling

In order to make a qualitative estimate of the relative amounts of ^{129}I in the various compartment shown schematically in Figure 10, certain assumptions have been made:

- a) the amount of ^{129}I entering and leaving the flow system has been constant over the 35 years that Area C has been in operation.
- b) the thickness of the plume is 1 m, length 285 m, porosity 0.4, rate of flow 0.25 m/day
- c) the total volume of sands in plume zone between recharge and discharge is $5.2 \times 10^4 \text{ m}^3$; volume of peats at discharge zone is $3.9 \times 10^3 \text{ m}^3$
- d) the area of the discharge zone enclosing the 10 Bq/g C contour is approximately $4 \times 10^4 \text{ m}^2$

e) the total biomass of the area is approximately 12 kg/m^2

f) the height of the air mass containing heightened ^{129}I levels is approximately 3 m (total height of canopy approximately 10 m)

g) the rate of air turnover immediately above the swamp is approximately once per day

Using these approximations, and the measured ^{129}I concentrations in Tables 8 and 9, the following estimates are possible:

	<i>Atoms ^{129}I</i>	<i>% Total Input</i>
<i>Total recharge input</i>	4×10^{20}	100
Total on sand particles along flow path	5.1×10^{19}	13
Total discharge	3.8×10^{19}	9.5
Total on peats	2.4×10^{19}	6.0
Total in plants	7.3×10^{19}	18
Total in air	1.2×10^{16}	<u><0.01</u>

Total accounted for: 46

It is to be noted here that the results of the empirical model are based on estimated areas and volumes only.

5 SUMMARY AND CONCLUSIONS

5.1 Geochemistry

The groundwaters throughout the flow system are characterized by Na-Ca/Cl-HCO₃ geochemical facies with little distinction between groundwaters in the recharge area near Area C and the discharge area along Duke Swamp. The origin of the NaCl source for some areas may be road salt, although additional Na⁺ sources exist, and cation exchange for Ca²⁺ plays a role. Cross-

correlation of ^3H (defining Area C plume) with other geochemical species provides no statistical evidence that any major geochemical species are derived from the waste compound.

Groundwaters show little variation in pH, averaging 5.7 with acidity attributed to soil and subsurface sources of CO_2 (Log P_{CO_2} from -1.29 to -2.38). $\delta^{13}\text{C}_{\text{DIC}}$ indicate microbially respired CO_2 with minimal dissolution of carbonate minerals. Groundwaters are highly undersaturated with calcite (log $\text{SI}_{\text{cal}} = -3.3$ to -3.5), but close to saturation with respect to amorphous silica, indicating little alteration along the flow path and little buffering of CO_2 acidity.

All groundwaters have elevated DOC (8 to 26 mg-C/L); the source may be a combination of organic waste from Area C, ^{14}C -active organics leached from soils in the vicinity of Area C, and sedimentary organic material within the late Quaternary sands. Given the high ^{14}C -activity of the dissolved carbon much of this DOC must be derived from recharge through and adjacent to Area C. Nitrate, sulphate and dissolved iron distributions indicate strong heterogeneity in redox conditions, possibly controlled by distribution of permeability in the aquifer.

5.2 Iodine

This field study has provided the first in-situ measurements of ^{129}I adsorption on aquifer materials (sand, sandy silt and peats), and the first tentative indication that the volatilization of iodine present in upwelling groundwaters can occur in discharge zones. Vegetative uptake of this gaseous iodine may subsequently be more significant than that of root uptake.

While the iodine behaviour appears to mimic that of tritium, and hence has been interpreted as conservative, the reasons for a ten fold reduction between recharge and discharge noted in both cases are probably very different. In the case of tritium the chief reasons for the decline in specific activity are a known reduction in the amounts being buried at Area C, and decay over the 3 to 4 year transit time from recharge to discharge. In the case of ^{129}I we have no reason to suspect a decrease in leaching of this isotope from the waste site, and the influence of decay is negligible.

A qualitative estimate of the inventories of this radioisotope in the various sinks existing along the flow path indicate that as much as 19% of the total ^{129}I input may be sorbed by aquifer materials with a further 18% taken up by vegetation in the discharge area.

6 RECOMMENDATIONS FOR ADDITIONAL WORK

Based on the results of this study the following recommendations are proposed:

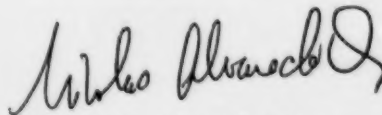
- 1) Identify improved method for measuring stable iodine at <0.1 ppb levels, including an examination of gas chromatographic and spectrophotometric methods.
- 2) Increase our knowledge of the ranges of concentration of stable I and ^{129}I in the environment, by measuring precipitation and air in the vicinity of CRL, surface waters (Ottawa River - above and below CRL) and a groundwater profile in a region of vertical recharge well beyond the influence of reactor operations (Sturgeon Falls, Ontario). The latter should provide an indication of the residual ^{129}I deposited during weapons testing in 1950s and '60s, and the extent of its long term sorption on both organic and sandy media.
- 3) Determine the form of the iodine present in these groundwaters (inorganic I or organically bound, complexed I etc.)
- 4) Determine the form of the iodine present in the air at Duke Swamp (inorganic or organic)
- 5) Better characterization of the DOC present in the groundwater, to determine its origin (soils, waste organics from site C, buried peat in the sand aquifer) and its ^{129}I -activity (for (2) above).

6) The groundwater chemistry appears rather heterogeneous along the flow path. Additional monitoring of a broader network of piezometers, together with (4) would constrain the geochemical evolution of the groundwaters along the flow path and allow flowpath modelling using a code such as NETPATH.

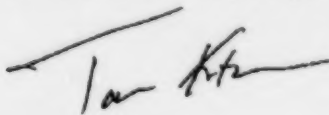
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7 REFERENCES

- Amiro, B.D., Sheppard, S.C. and Sheppard, M.I. (1993). Iodine transfer through the soil - plant - atmosphere continuum. *Radioactive Waste Management*, 124-129
- Ball, J.W. and Nordstrom, D.K. (1991). *User's manual for WATEQ4F, with revised thermodynamic database and text cases for calculating speciation of major, trace and redox elements in natural waters*. U.S. Geological Survey Open File Report 91-183.
- Beaujean, H., Bohenstingl, J., Laser, M., Merz, E. and Schnez, H. (1973). Gaseous radioactive emissions from reprocessing plants and their possible reduction. Environmental Behaviour of Radionuclides Released in the Nuclear industry. IAEA-SM-172/17.
- Behrens, H. (1982). New insights into the chemical behaviour of radioiodine in aquatic environments. *Environmental Migration of Long-Lived Radionuclides*. IAEA-SM-257/36, IAEA, Vienna.
- Bird G.A. & Schwartz, W. (1996). Distribution coefficients, K_d 's, for iodide in Canadian Shield Lake sediments under oxic and anoxic conditions. *J. Environ. Radioactivity*, 35 (3), pp.261-279.
- Brauer, F.P. and Ballou, N.E. (1975). Isotopic ratios and other radionuclides as nuclear power pollution indicators. Isotopic Ratios as Pollutant Source and Behaviour Indicators. IAEA-SM-191/20.
- Brauer, F.P. and Kaye, J.H. (1974). Detection systems for the low level radiochemical analyses of ^{131}I , ^{129}I and natural I in environmental samples. *IEEE Transactions, Nuclear Science*, NS21 (1), pp. 496-502.
- Chant, L. A., Andrews, H.R., Cornett, R.J., Koslowsky, V., Milton, J.C.D., Van Der Berg, G.J., Verburg, T.G. and Wolterbeek, H.TH. (1996). ^{129}I and ^{36}Cl concentrations in lichens collected in 1990 from three regions around Chernobyl. *Appl. Radiat. Isot.* 47 (9/10), pp.933-937.
- Cornett, R.J., Chant, L., Andrews, H.R., Davies, W.G., Greiner, B.F., Imahori, Y., Koslowsky, V.T., Kotzer, T.G., Milton, J.C.D., Milton, G.M. (1997). ^{36}Cl and ^{129}I in teeth and bones. *Nucl.Instr.Meth.Phys.Res.*, B123, pp.249-253.
- Coughtrey, P.J., Jackson, D. and Thorne, M.C. (1983). In Radionuclide Distribution and Transport in Terrestrial and Aquatic Ecosystems - A Critical Review of Data. Vol.3 AABalkema / Rotterdam.
- Elmore, D., Fulton, B., Clover, M., Marsden, J., Gove, H., Naylor, K., Purser, K., Kilius, L., Beukens, R. and Litherland, A. (1979). Analysis of ^{36}Cl in environmental water samples using an electrostatic accelerator. *Nature*, 227, pp.22-25.

- Elmore, D., Gove, H.E., Ferraro, R., Kilius, L.R., Lee, H.W., Chang, K.H., Beukens, R.P., Litherland, A.E., Russo, C.J., Purser, K.H., Murrell, M.T. and Finkel, R.C. (1980). Determination of ^{129}I using tandem accelerator mass spectrometry. *Nature*, **286**, pp.138-140.
- Evans, G.J. & Hammad, K.A. (1995). Radioanalytical studies of Iodine behaviour in the environment. *Journal of Radioanalytical and Nuclear Chemistry*. **192** (2), pp.239-247.
- Delmore, J.E.(1982). Isotopic analysis of iodine using negative surface ionization. *International Journal of Mass Spectrometry and Ion Physics*, **43** (4), pp. 273-281.
- Evendon, W.G., Sheppard, S.C. and Killey, R.W.D. (1998). Carbon-14 and tritium in plants of a ground-water contaminated wetland. *Applied Geochemistry* **13**, pp. 17-21.
- Fabryka-Martin, J., Bentley, H., Elmore, D. and Airey, P. (1985). Natural Iodine-129 as an environmental tracer. *Geochimica et Cosmochimica Acta.*, **49**, pp.337-347.
- Fabryka-Martin, J. (1988). Production of radionuclides in their earth and their hydrogeologic significance, with emphasis on Chlorine-36 and Iodine-129. PhD thesis, University of Arizona: 400 pages.
- Fabryla-Martin, J. and Davis, S. (1987). Applications of ^{129}I and ^{36}Cl in hydrology. *NIMB* **29**, pp361-371.
- Fabryka-Martin, J., Davis, S., Elmore, D. and Kubik, P. (1989). *In-situ* production and migration of ^{129}I in the Stripa Granite, Sweden. *Geochimica et Cosmochimica Acta*. **53**, pp.1817-1823.
- Fehn, U., Holden, G.R., Elmore, D., Brunelle, T., Teng, R. and Kubik, P. (1986). Determination of natural and anthropogenic ^{129}I in marine sediments. *Geophysical Research Letters*. **13** (1), pp.137-139.
- Fehn, U., Tullai, S., Teng, R., Elmore, D. and Kubik, P. (1987). Determination of ^{129}I in heavy residues of 2 crude oils. *Nuclear Instruments and Methods in Physics Research*. **B29**, pp.380-382.
- Fehn, U., Tullai-Fitzpatrick, S., Teng, R., Gove, H., Kubik, P., Sharma, P. and Elmore, D. (1990). Dating of oilfield brines using ^{129}I . *Nuclear Instruments and Methods in Physics Research* **B52**, pp.446-450.
- Fehn, U., Peters, E.K., Tullai-Fitzpatrick, S., Kubik, P., Sharma, P., Teng, R., Gove, H. and Elmore, D. (1992). ^{129}I and ^{36}Cl concentrations in waters of the eastern Clear Lake area, California: Residence times and source ages of the hydrothermal fluids. *Geochimica et Cosmochimica Acta*. **56**, pp.2069-2079.

Fuge, R. & Johnson, C.C. (1986). The geochemistry of iodine- A review. *Environmental Geochem. Hlth.* **8**, pp.31-54.

Gascoyne, M and Kotzer, T.G. (1995). Isotopic methods in hydrogeology and their application to the Underground Research Laboratory, Manitoba. *AECL-11370*, 101 pages.

Handl, J., Oliver, E., Jakob, D., Johanson, K.J. and Schuller, P (1993). Biospheric ^{129}I concentrations in the pre-nuclear and nuclear age. *Health physics*, **63** (3), pp. 265-271.

Killey, R.W.D., Rao, R.R. & Eyvindson, S. (1993). Radiocarbon speciation and distribution in an aquifer plume and groundwater discharge area, Chalk River Ontario. *AECL 1135*. Atomic Energy of Canada Limited, Chalk River, Ontario K0J 1J0, Canada

Killey, R.W., Rao, R.R. and Eyvindson, S. (1998). Radiocarbon Speciation and Distribution in an Aquifer Plume and Groundwater Discharge Area, Chalk River, Ontario. *Applied Geochemistry*. **13**, pp.3-16.

Kotzer, T., Gascoyne, M., Mukai, M., Ross, J., Waito, G., Milton, G. and Cornett, R.J. (1999). ^{36}Cl , ^{129}I and Noble Gas Isotope Systematics in Groundwaters from the Lac Du Bonnet Batholith, Manitoba, Canada. *Radiochimica Acta*, In press.

Koslowsky, V.T., Andrews, H.R., Davies, W.G. and Murnaghan, K. (1997). The Chalk River AMS Time-of- Flight Detection System. *N.I.M.B.* **123**, pp144-147

Koslowsky, V.T., Bray, N., Imahori, Y., Andrews, H.R. and Davies, W.G. (1997). The New Chalk River Ion Source, Sample Changer and External Sample magazine. *N.I.M.B.* **123**, pp 203-207.

Krestow, J.S.A (1996). Use of *Dreissena Polymorpha* for ^{129}I determinations in eastern Canada by accelerator mass spectrometry. *Unpublished Thesis, University of Toronto*, 77 pages.

Leiser, K.H. & Steinkopff, TH. (1989). Chemistry of radioactive iodine in the Hydrosphere and in the Geosphere. *Radiochimica Acta*. **46**, pp.49-55.

McHugh, J. and Sheffield, J. (1965). Mass analysis of sub-nanogram quantities of iodine. *Analytical Chemistry*, **37**, pp. 1099-1101.

Milton, G.M., Andrews, H.R., Causey, S.E., Chant, L.A., Cornett, R.J., Davies, W.G., Greiner, B.F., Koslowsky, V.T., Imahori, Y., Kramer, S.J., McKay, J.W. and Milton, J.C.D. (1994). Chlorine-36 dispersion in the Chalk River Area. *N.I.M.B.*, **B92**, pp.376-379.

Milton, G.M., Kramer, S.J., Brown, R.M., Repta, C.J.W., King, K.J. and Rao, R.R. (1995). Radiocarbon dispersion around Canadian nuclear facilities. *Radiocarbon*, **37** (2), pp. 485-496.

- Milton, G.M., King, K.J., Sutton, J. and Enright S. (1998). Tracer studies of carbon source and utilization in a wetland on the Canadian Shield. *Applied Geochemistry* **13**, pp.23-30.
- Muramatsu, Y. & Ohmomo, Y. (1986). Iodine-129 and iodine -127 in environmental samples collected from Tokaimura/Ibaraki, Japan. *The Science of Total Environment*. **48**, pp.33-43.
- Muramatsu, Y., Uchida, S., Sriyotha, P. & Sriyotha, K. (1990). Some considerations of the sorption and desorption phenomena of iodide and iodate on soil. *Water, Air and Soil Pollution*. **49**, pp.125-138.
- NCRP Report (1983). Iodine-129: Evaluation of release from nuclear power generation. Report No 75.
- Noack, M.H. (1995). Estimating groundwater velocity for shallow unconfined aquifer using the $^3\text{H}/^3\text{He}^*$ dating technique: A comparison to other hydrogeologic methods. M. Sc. Thesis, Trent University: 138 pages.
- Paquette, J. and Kupferschmidt, W.C.H. (1986). The Chemistry of Iodine. Canadian Nuclear Society Technical Supplement, Bulletin Sept/Oct.
- Rahn, K.A., Borys, R.D. and Duce, R.A.. (1977). Determination of Inorganic and Organic Components of Gaseous Chlorine, Bromine and Iodine in the Atmosphere. In: *Proceedings of the Meteorological Organization on Technical Conference on Air Pollution Measurement Techniques*, Gothenburg, Sweden October 11-15.
- Ross, J. and Gascoyne, M (1995). Methods for sampling and analysis of groundwaters in the Canadian Nuclear Fuel Waste management Program. AECL Tech. Report TR-588, COG-93-36.
- Sheppard, M.I., Thibault, D.H. & Smith, P.A. (1989). Iodine dispersion and effects on groundwater chemistry following a release to a peat bog, Manitoba, Canada. *Applied Geochemistry*. **4**, pp.423-432.
- Sheppard, M.I. and Thibeault, D. H. (1990). Default soil solid/liquid partition coefficients, K_d s for four major soil types; a compendium. *Health Physics* Vol. 59, No 4, pp 471-482
- Stephenson, M. and Motyka, M. (1994). Review and assessment of methods for the measurement and speciation of iodine in fresh water. *AECL Report TR 631*, COG 94-64.
- Stoffels, J.J. (1982). Measurement of Iodine-129 at the femtogram level by negative surface ionization mass spectrometry. *Radiochemical and Radioanalytical Letters*, **55** (2), pp. 99-106.
- Tessier, A., Campbell, P.G.C. & Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry*. **51** (7), June.

Whitehead, D.C. (1984). The distribution and transformations of iodine in the environment. *Environment International*. **10**, pp.321-339.

Wyttenbach, A., Bajo, S., Furrere, V., Langenauer, M. and Tobler, L. (1997). Accumulation of arsenic, bromine and iodine in needles of Norway Spruce (*Picea Abies* [L.] Karst.) at sites with low pollution. *Water, Air and Soil Pollution*, **94**, pp. 417-430.

Table 1 Stable iodine concentrations measured in a variety of terrestrial materials

Sample type	Range of I concentrations
fresh water	0.5 – 20 µg/L
oceanic water	45 – 60 µg /L
precipitation	0.5 - 5 µg/L
soils	0.5 – 20 mg/kg
peat	20 – 100 mg/kg
coal	1 - 15 mg/kg
sedimentary rock	3 – 400 mg/kg
igneous rock	0.2 – 1.2 mg/kg
algae	50 – 2500 mg/kg
lichens	2 – 5 mg/kg
tree leaves, needles	0.2 – 6.9 mg/kg
fresh water fish	0.05 – 0.2 mg/kg
marine fish	0.5 – 6 mg/kg
human thyroid tissue	1 – 3 mg/kg

These data have been abstracted from a number of sources in the literature, including Coughtrey et al. (1983), Whitehead (1984), Fuge and Johnson (1986). In many cases they are based on a rather small sample set.

Table 2 Methods for trace measurements of stable iodine

Analytical Technique	Lower Limit of Detection
neutron activation analysis	0.1 – 1 µg/L
ion selective electrode	0.1 µg/L
gas chromatography	0.1 µg/L
high performance liquid chromatography	0.15 µg/L
polarography	0.025 – 1 µg/L
catalytic spectrophotometry	1µg/L
inductively coupled plasma/ mass spectrometry	0.2 µg/L

This material has been abstracted from Stephenson and Motycka (1994)

Table 3 Concentration of ^{129}I and $^{129}\text{I}/\text{I}$ ratios for precipitation, surface waters and brines

I) Pre-bomb background values(1)	¹²⁹ I (atoms/L)	¹²⁹ I / I (x10 ⁻¹³)
Average meteoric waters		6
Meteoric waters (Great Artesian Basin)		5.7
Seawater		12
Germany+Isreal (pre-Chernobyl)	10 ⁷	
II)Post-bomb values(1,2,3)		
Average meteoric waters		10 to 1000
Deep River precipitation	2.5x10 ⁸	0.52
CRL - near stack (snow)	2.2x10 ⁹	470
Germany+Isreal (Chernobyl fallout)	10 ⁹ to 10 ¹⁰	
Lac du Bonnet Batholith (shallow recharge)		2600
Surface waters - Algonquin Highlands	1.18x10 ⁸	50,000
III) Fresh to saline groundwaters from the Stripa granite ⁴		
Description		
shallow groundwaters	0.02x10 ⁷	160
shallow mine waters	.13-.27x10 ⁷	410-520
deep mine waters	3.2-20.0x10 ⁷	70-2400
IV) Crude oils ⁵ and saline oil-field brines ⁶		
Sample	Formation age	
Oilfield brines		
WCBB	Miocene	2.59
Newton	Jurassic	0.72
Aneth 1	Pennsylvanian	8.34
Aneth 11	Pennsylvanian	4.34
Crude Oils		
Monterrey oil		54.0-62.0
Source rocks		41.0
San Juan oil		100
Source and reservoir rocks		1.0-6.0

Remarks

1. Summarized from Gascoyne and Kotzer (1995)
2. Krestow (1996)
3. G. Milton (personal communication)
4. data summarized from Fabryka-Martin et al.(1989)
5. Fehn et al.(1990)
6. Fehn et al.(1987)

Table 4 Selected K_D values in the published literature (laboratory experiments only)

Soil Type	Soil/Water Ratio	Measured K_D	Reference
sand	1/10	1 (0.04-81)	Sheppard and Thibeault (1990 - compilation)
loam	"	5 (0.1-43)	
clay	"	1 (0.2-29)	
organics	"	25 (1.4-368)	
sand	1/100	0.1	Bird and Schwartz (1996)
clay	"	32	
organics	"	247	
organics	1/10	5.2-8.1	
sand-humus	1/4 - 1/8	36 -73	Bors et al. (1991)
clay-silt	"	27 - 317	
sand	1/10	35	Muramatsu et al. (1990)
field	"	7500	
paddy	"	560	
lake seds	1/100	360-600	Evans and Hammad (1995)
clay	"	1.3 - 5	

Table 5a Groundwater geochemistry and piezometer details

Site	Depth m	Water m b.g.s.	pH	T °C	Alk. HCO ₃ ⁻	DOC mg-C/L	Cl ⁻ mg/L	SO ₄ ²⁻ mg/L	NO ₃ ⁻ mg/L	Ca ²⁺ mg/L	Mg ²⁺ mg/L	Na ⁺ mg/L	K ⁺ mg/L	Fe _{tot} mg/L	Si mg/L	P _{CO₂} (Log)	LogSI Cal.	LogSI Am Si.
<i>Recharge</i>																		
C14-1(7)	7	6.5	5.64	12.2	13.42	11.09	672.00	37.60	<0.05	43.39	12.42	292.59	8.33	33.11	5.59	-1.60	-3.26	-1.19
C14-2(8.5)	8.5	6.5	5.84	12.0	3.28	9.49	290.00	63.00	<0.05	11.43	2.98	180.56	4.89	7.33	4.29	-2.41	-4.26	-1.30
C111-8	8	8	5.90	12.1	14.55	12.31	84.60	1.40	<0.05	10.45	3.04	46.11	3.81	18.15	5.12	-1.80	-3.48	-1.23
C111-11	11	8	5.50	12.2	2.44	9.33	86.90	15.80	38.29	9.55	2.52	41.94	4.74	<0.01	5.14	-2.18	-4.71	-1.23
C114-8 (10/97)	8	7	6.00	13.0	57.95	15.35	56.20	1.30	<0.05	15.45	3.12	59.63	3.76	0.01	5.57	-1.30	-2.61	-1.20
C114-11 (10/97)	11	7	5.70	12.4	4.37	16.49	79.40	1.10	<0.05	9.46	2.32	40.46	2.36	6.47	5.38	-2.12	-4.23	-1.21
<i>Intermediate</i>																		
C8-2	14m	7.5	5.78	11.0	28.06	8.28	71.80	15.90	7.03	14.91	3.62	45.93	4.68	0.10	6.48	-1.41	-3.20	-1.12
C8-3	11.5	7.5	5.60	11.0	30.50	7.88	25.00	13.10	1.17	12.95	3.14	13.89	7.74	0.12	7.46	-1.19	-3.37	-1.05
C23-II	10	8.5	5.59	11.0	16.80	11.79	81.40	12.40	<0.05	9.55	2.59	47.31	3.11	4.02	5.47	-1.44	-3.79	-1.19
<i>Discharge</i>																		
C213-4	4	4	5.93	15.5	33.50	17.07	36.90	10.30	2.20	13.21	3.16	19.17	3.49	56.58	5.87	-1.45	-2.93	-1.21
C213-8	8	4	5.92	11.0	92.72	11.44	10.14	8.90	<0.05	23.93	6.44	23.80	2.32	0.25	5.52	-1.03	-2.32	-1.19
C221-7	7	6	5.20	9.5	0.92	11.18	93.20	21.60	2.32	6.62	1.45	6.81	1.56	0.18	5.69	-2.31	-5.61	-1.16
C221-9	9	6	5.49	9.5	3.34	13.34	98.00	19.20	<0.05	20.27	5.44	51.20	2.70	0.22	6.00	-2.05	-4.31	-1.13
C221-16	16	6	6.15	10.0	11.91	13.58	93.00	0.80	<0.05	12.95	4.20	29.07	3.31	38.72	7.07	-2.15	-3.26	-1.07
C210	Art.		6.22	13.0	84.78	24.49	51.30	0.60	<0.05	16.25	5.58	19.07	3.09	42.90	11.20	-1.36	-2.22	-0.90
C35	9	3.1	5.04	9.50	117.80	25.61	n/a	n/a	n/a	13.08	3.71	4.26	1.16	0.27	5.70	-0.04	-3.36	-1.16
DSR	0		6.15	17.0	24.89	14.90	44.00	0.80	<0.05	15.36	5.19	17.41	1.55	2.04	8.22	-1.79	-2.74	-1.08

n/a – not analysed

Table 5b Environmental isotope analyses and selected ion ratios for groundwaters

	pH	DOC mg-C/L	Alk HCO ₃ ⁻	DIC mg-C/L	Na/Ca (meq)	Na/Cl (meq)	TDS mg/L	$\delta^{13}\text{C}$ DIC	³ H Bq/ml	¹⁴ C Bq/ml	¹⁴ C Bq/mg-C
Recharge											
C14-7	5.64	11.1	13.4	20.1	5.9	0.67	912	-20.0	104.0	1.2	38.5
C14-8.5	5.84	9.5	3.3	3.3	13.7	0.96	516	-20.2	31.0	0.62	48.3
C111-8	5.90	12.3	14.6	13.3	3.8	0.84	158	-21.4	0.3	0.33	12.9
C111-11	5.50	9.3	2.4	4.9	3.8	0.74	185	-19.9	54.0	0.68	47.9
C114-8(10/97)	6.00	15.4	58.0	44.3	3.4	1.64	225	-21.6	33.0	0.63	10.6
C114-8(07/98)									342 ¹		
C114-11	5.70	16.5	4.4	5.8	3.7	0.79	130	-20.3	0.4	0.33	14.8
Intermediate											
C8-2	5.78	8.3	28.1	31.9	2.7	0.99	192	-19.5	76.0	0.93	23.1
C8-3	5.60	7.9	30.5	49.5	0.9	0.86	114	-21.0	28.0	0.67	11.7
C23-11	5.59	11.8	16.8	27.8	4.3	0.90	166	-19.6	8.3	0.4	10.1
Discharge											
C213-4	5.93	17.1	33.5	28.9	1.3	0.80	121	-9.9	65.0	1.08	23.5
C213-8	5.92	11.5	92.7	81.5	0.9	3.62	194	-18.6	159.0	1.13	12.2
C221-7	5.20	11.2	0.9	3.5	0.9	0.11	74	-18.6	5.9	0.42	28.7
C221-9	5.49	13.3	3.3	6.8	2.2	0.81	187	-20.8	200.0	1.5	74.5
C221-16	6.15	13.6	11.9	7.1	2.0	0.48	129	-21.1	0.6	0.37	17.9
C35	5.04	25.6	117.8	632.7	0.3		140	-12.9	0.0	0	0.0
CO4	6.22	24.5	84.8	45.7	1.0	0.57	175	-17.4	257.0	2.57	36.6
DSR	6.15	14.9	24.9	14.9	1.0	0.61	105	-15.5	99.0	1.13	37.9

¹ tritium value for groundwater sampled in 07/98

Table 6 ^{129}I values for groundwater samples

Samples	Total Iodine (ng/ml)	Dilution	Measured $^{129}\text{I}/^{127}\text{I}$ (Bkgd subtracted)	$^{129}\text{I}/^{127}\text{I}$ dilution Corrected	^{129}I (atoms/l) ¹ Corrected
Recharge					
C14-1(7)	0.72	139001	3.50E-12		1.66E+09
C14-2(8.5)	0.59	169340	2.89E-12		1.37E+09
C111-8	2.00	50001	2.48E-12		1.18E+09
C111-11	7.30	13700	2.07E-12		9.83E+08
C114-8 (May97)	67.	*149.3	4.80E-09	7.20E-07	2.30E+11
C114-8 (Oct97)	6.88	14536	1.27E-10		6.03E+10
C114-8 (July98)	49.00	*1367	2.61E-09	3.56E-06	8.28E+11
C114-11(Oct97)	2.17	46306	1.87E-12		8.93E+08
C114-11(July98)	2.50	26709	5.92E-12		1.88E+09
Intermediate					
C8-2	13.00	*7723	4.37E-11	3.37E-07	2.08E+10
C8-3	1.50	67097	6.06E-12		2.89E+09
C23-II	3.10	32392	9.97E-11		4.75E+10
Discharge					
C210-0.5 m(05/97)	32.4	*308.7	1.12E-09	3.40E-07	5.40E+10
C210-0.5 m(10/97)	26.00	*3847	1.77E-10	6.81E-07	8.40E+10
C210-6 m (05/97)	3.4	29412	8.78E-11		4.20E+09
C213-4	9.60	*10418	2.70E-11	2.81E-07	1.28E+10
C213-8	21.00	*4785	7.13E-11	3.41E-07	3.40E+10
C221-7	0.23	437937	2.14E-13		1.02E+08
C221-9	13.00	*7729	6.28E-10	4.85E-06	3.00E+11
C221-16	1.40	71738	1.53E-12		7.30E+08
C35	1.08	93021	1.35E-12		6.45E+08
DSR	12.00	*8334	3.85E-11	3.21E-07	1.82E+10

1. ^{129}I concentrations were calculated as follows. Following subtraction of the ^{129}I ratio measured in a "background" sample, the sample ratio was corrected for the dilution resulting from the addition of stable iodide. Atoms ^{129}I per litre or gram of sample were then calculated from this ratio. In cases where the dilution exceeded 10,000, the error so introduced made it impossible to calculate the dilution - corrected ratio with any precision. However, the atoms ^{129}I per litre could be calculated, assuming the total stable iodide present was 10 mg.

* Where dilutions were >10,000 values for atoms/L have been calculated on the assumption that the total stable iodine in the sample was equal to the carrier iodine added (10 mg). Only those marked with an asterisk have been dilution-corrected.

Total errors, including errors introduced by stable iodide measurement, are considered to be on the order of $\pm 20\%$ for ^{129}I measurements.

Table 7 Stable iodine and ^{129}I determinations for soil cores and leach solutions

Sample (depth interval)	treatment	stable I ng/g	^{129}I atoms/g soil
Core 114 A (4.6-5.1 m)	Combustion	198	3.2E+07
	MgCl ₂ leach	22	2.3E+06
	NH ₂ OH leach	-	2.8E+07
	KOH leach		1.7E+06
	total leaches		3.1E+07
Core 114 C (6.9-7.7 m)	Combustion	N.D.	9.0E+08
	MgCl ₂ leach	132	2.4E+08
	NH ₂ OH leach	-	1.4E+09
	KOH leach		5.8E+07
	total leaches		1.6E+09
Core 210 A (0-0.5m)	Combustion	15,600	4.3E+09
	MgCl ₂ leach	N.D.	5.9E+08
	NH ₂ OH leach	8800	1.3E+10
	KOH leach		2.9E+08
	total leaches	>8800	1.9E+10
Core 210 B (4.6-4.9 m)	Combustion	40	2.2E+07
	MgCl ₂ leach	93	8.1E+06
	NH ₂ OH leach	-	2.2E+07
	KOH leach		1.5E+06
	total leaches		3.2E+07

N.D. sample not submitted for measurement

- value reported below solution blank

As noted in the text the "blanks" for hydroxylamine hydrochloride were too high and variable to permit use of the measurements in all but one case.

Table 8 Summary of I and ^{129}I concentrations in soil leaches and co-existing groundwaters, with calculated values for K_D

Sample	Leachable I $\mu\text{g/kg}$	Leachable ^{129}I atoms/kg	Co-existing Groundwater atoms/L	K_D (L/kg)	
				^{129}I	I
114 A (sand)	< 200	3.0E+10	1.4E+09 (average)	21.4	n.d.
114 C (sand)	< 200	1.6E+12	2.9E+11 (average)	5.5	n.d.
210 A (peat) (0 – 0.5 m)	> 8800	1.9E+13	6.9E+10 (average)	273	303
210 B (sand) (4.6 – 4.9 m)	< 200	3.2E+10	4.2E+09	7.1	n.d.

Table 9 Summary of I and ^{129}I for selected vegetation and air samples taken at Duke Swamp

Sample	stable I	^{129}I concentration
groundwater discharge -C210	29 $\mu\text{g/L}$	$6.9 \times 10^{10} / \text{L}$
precipitation - C210 (est)	n.d.	$< 9 \times 10^8 / \text{L}$
air - C210 (3 day)	3 (est) ² ng/g	$2.0 \times 10^7 / \text{m}^3$
cedar - 0 exposure.(av of 3)	114 ng/g	$3.3 \times 10^7 / \text{g veg.}$
Potted cedar - 8 wks exp.	132 ng/g	$7.3 \times 10^7 / \text{g veg (- 0 exp.)}$
Planted cedar - 8 wks exp.	165 ng/g	$2.8 \times 10^8 / \text{g veg. (- 0 exp.)}$
in-situ lichen	200 (est) ¹ ng/g	$9.8 \times 10^8 / \text{g veg.}$

¹ based on information in Table 1

² based on information in Rahn et al. (1977)

n.d. - not determined

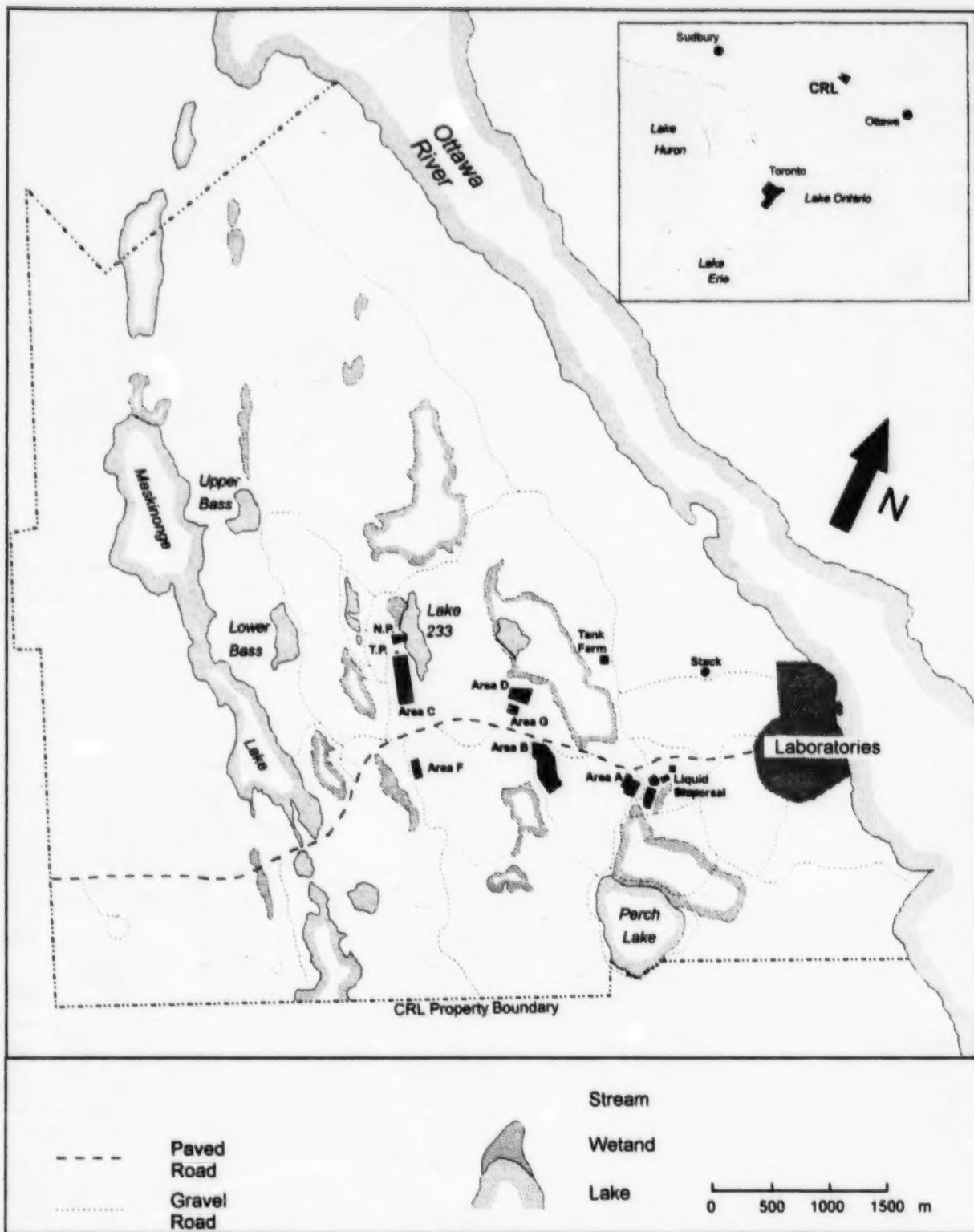


Figure 1 Geographic location of the Chalk River Laboratories (CRL), and the position of Waste Management Area "C"

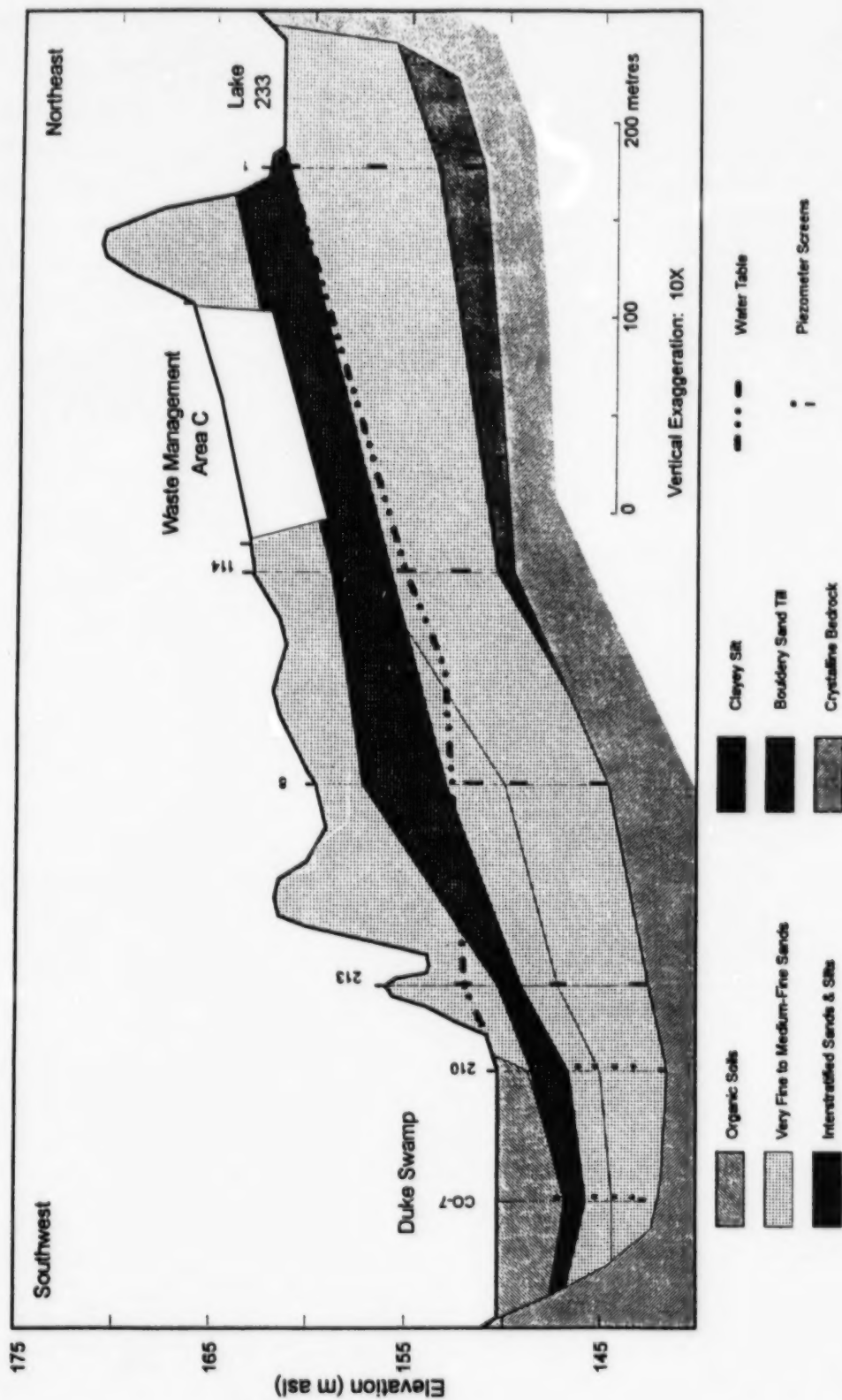


Figure 2 Stratigraphic section oriented parallel to the groundwater flow

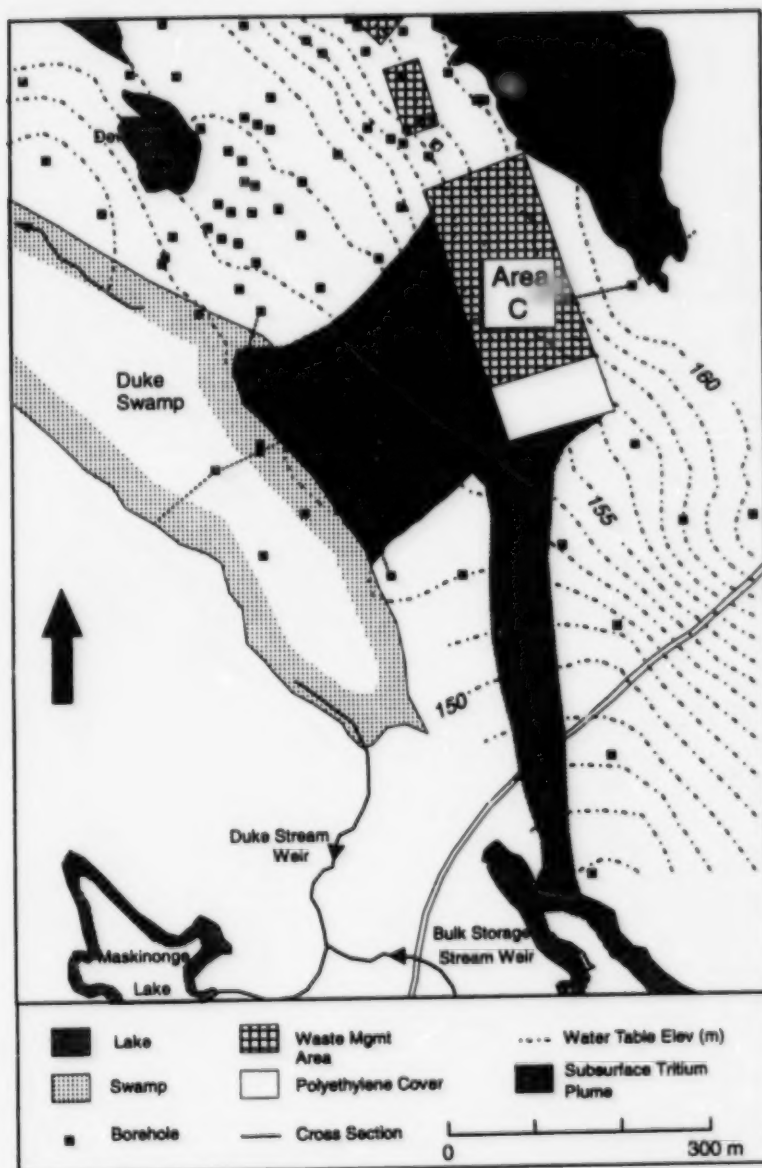


Figure 3: Piezometric grid of Area C

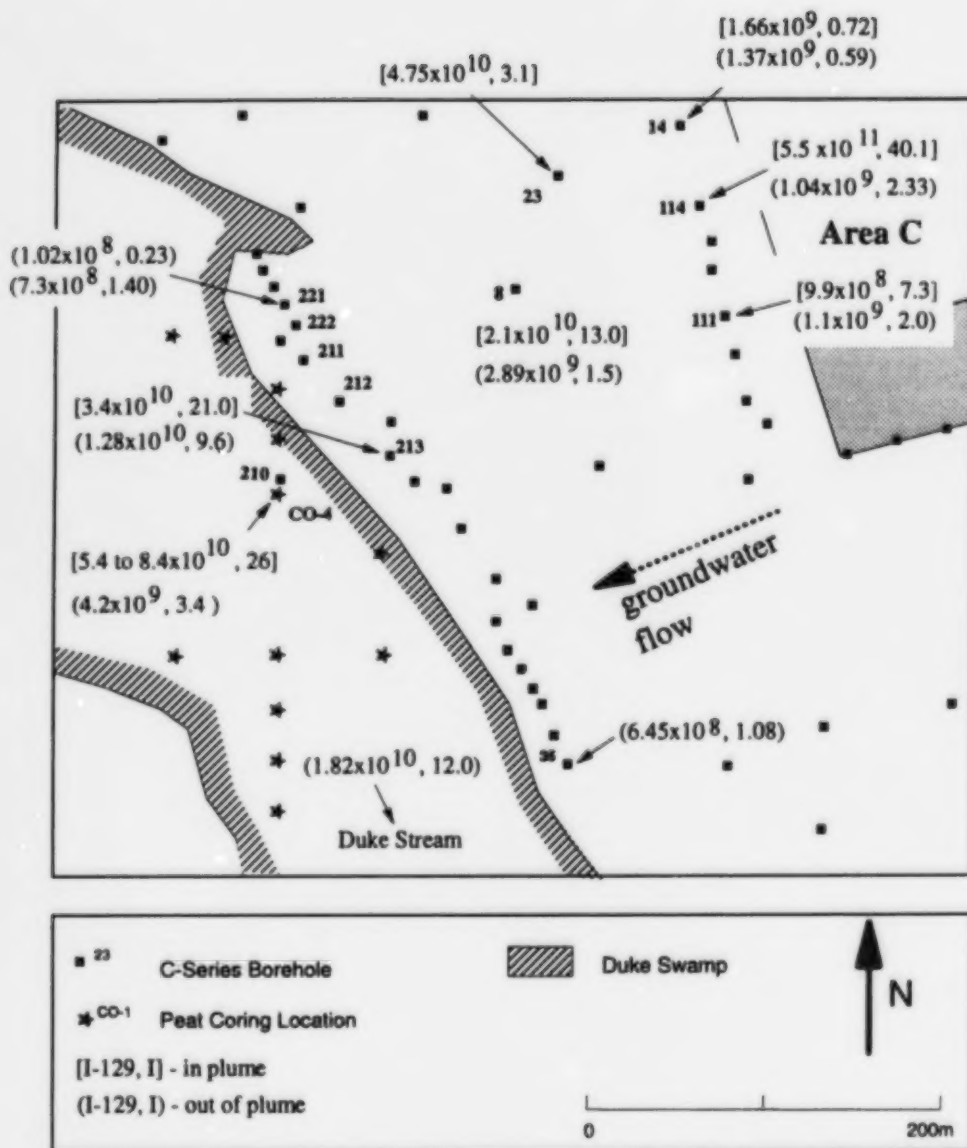


Figure 4: Spatial distribution of I and I-129 in groundwaters sampled from Area C.

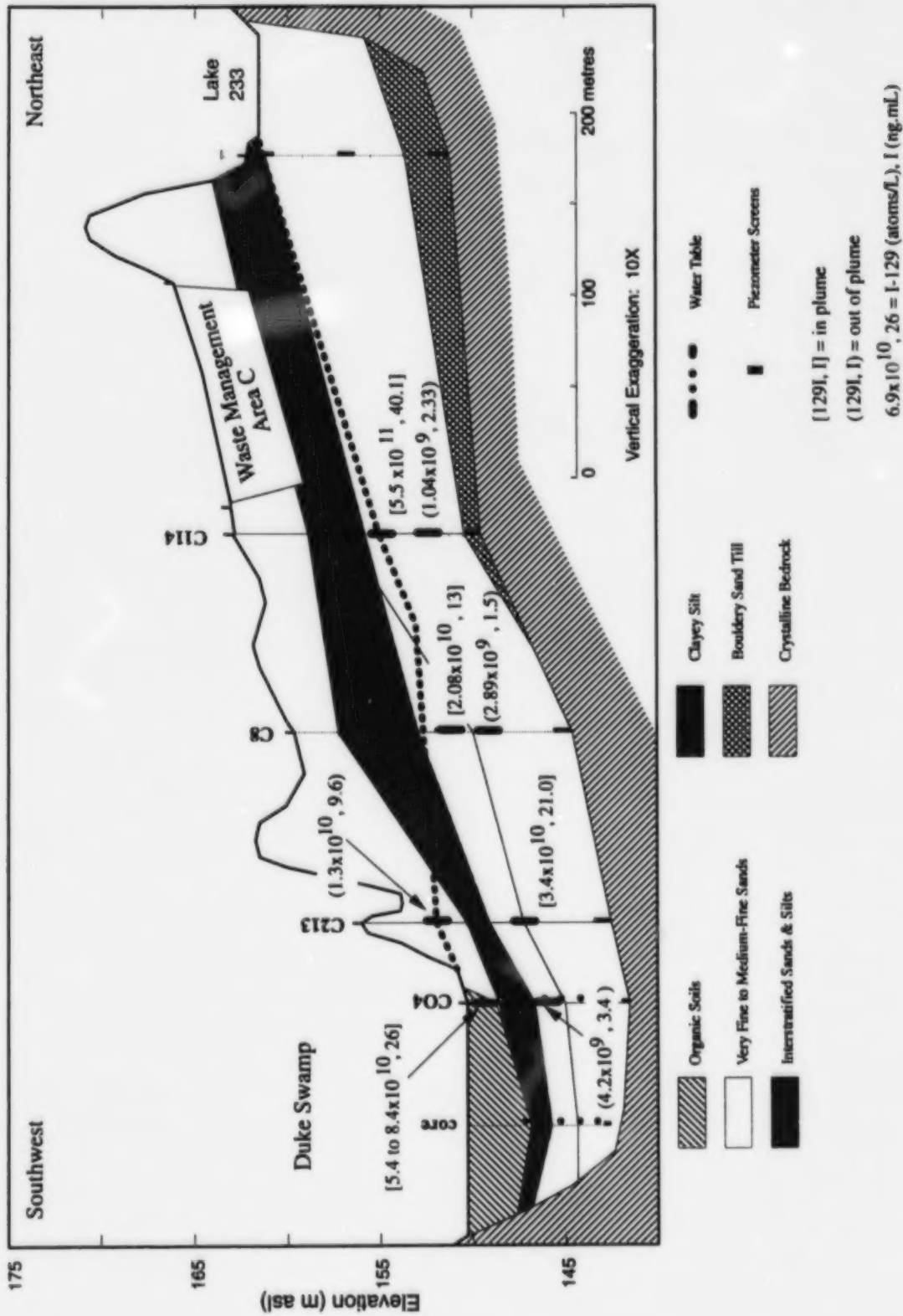


Figure 5. Changes in I and I-129 downgradient from Area C (data from Table 7).

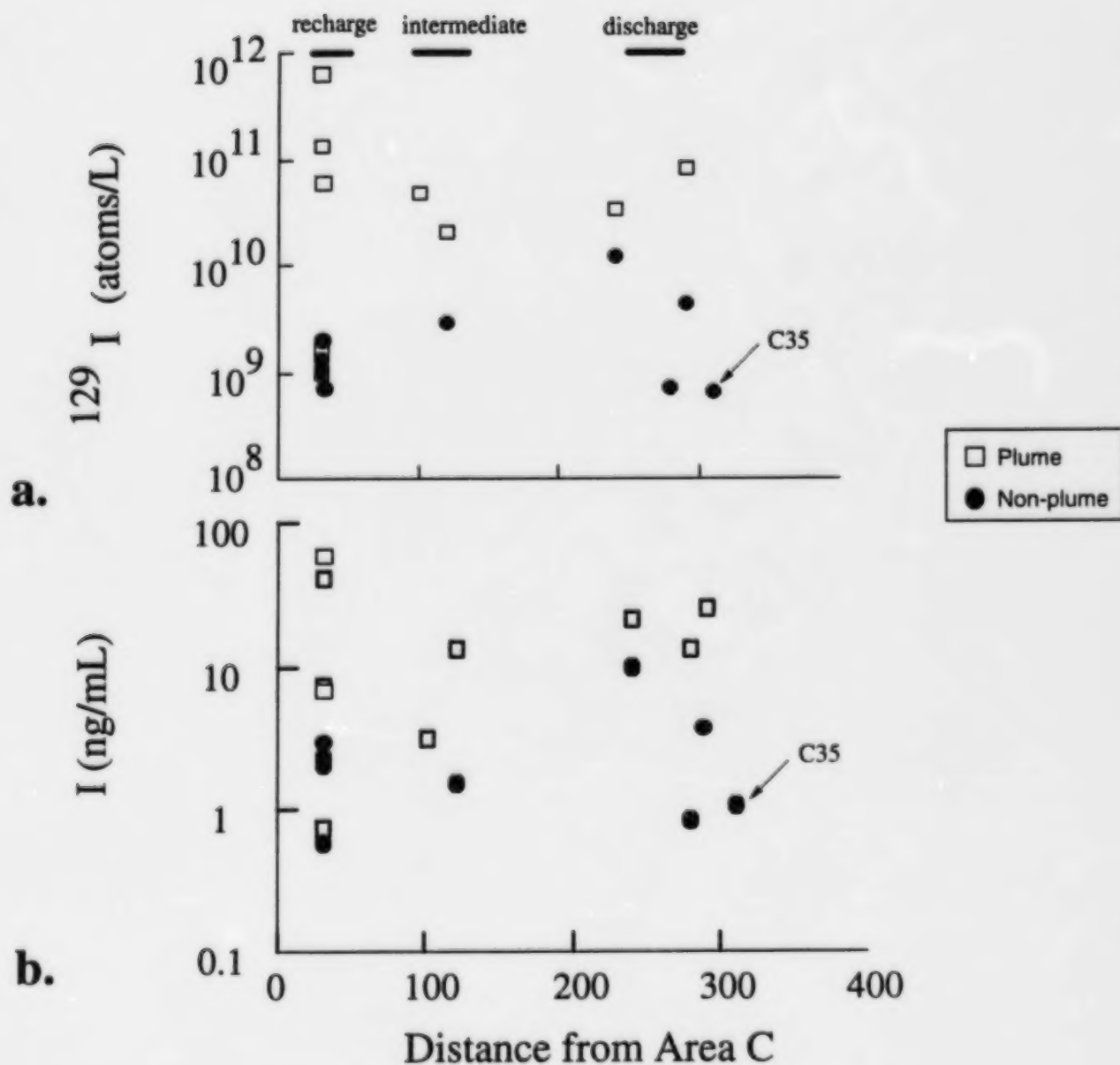


Figure 6: Changes in a) I-129 and b) stable I with increasing distance from Area C

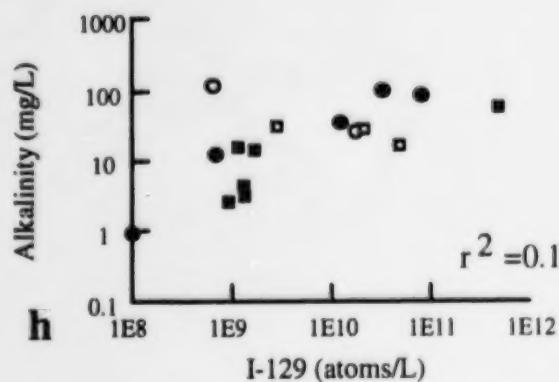
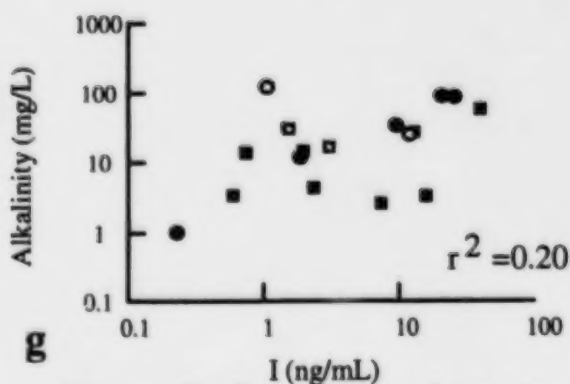
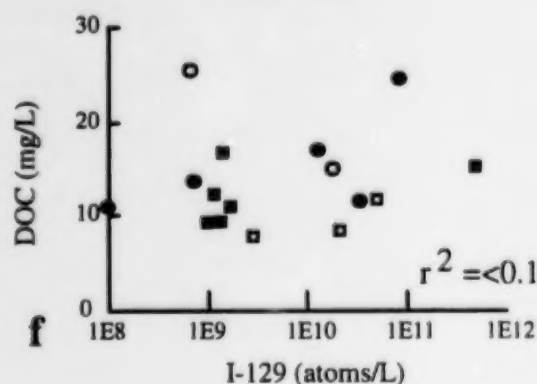
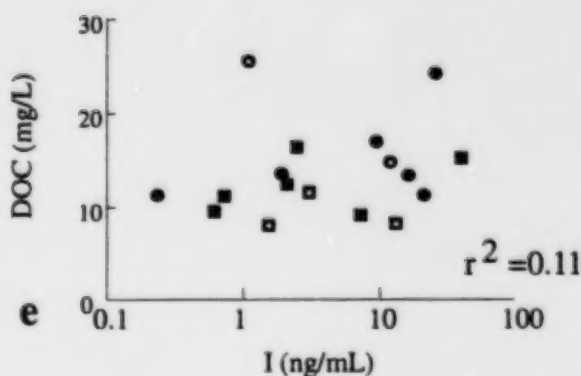
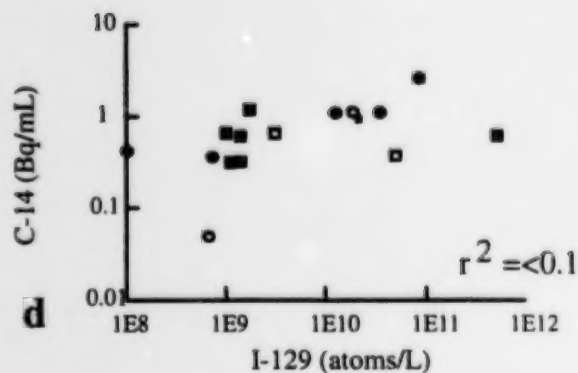
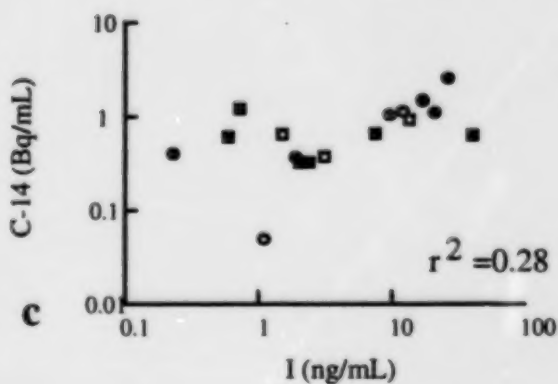
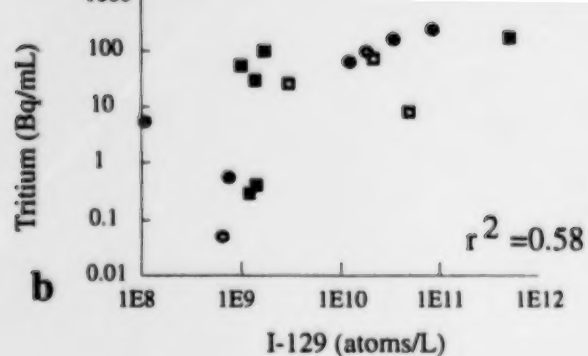
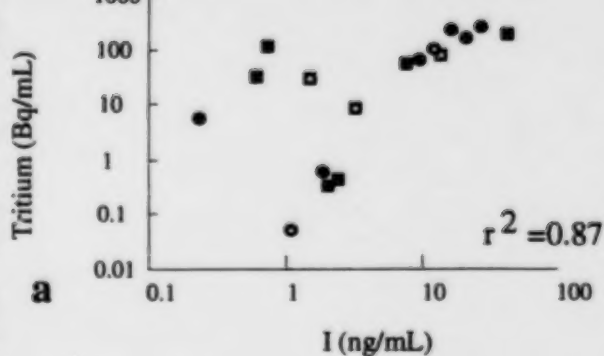


Figure 7. Correlation between I, I-129, radio-nuclides and chemical species in all groundwaters

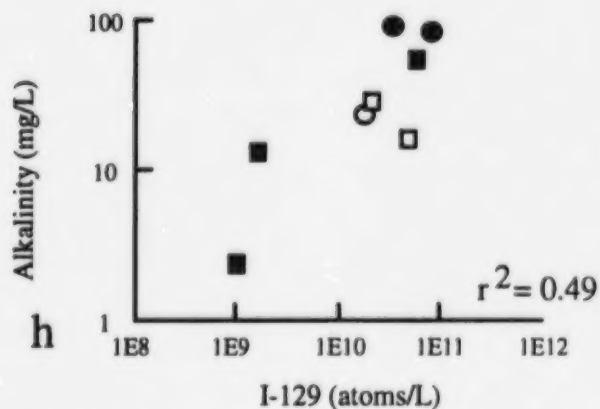
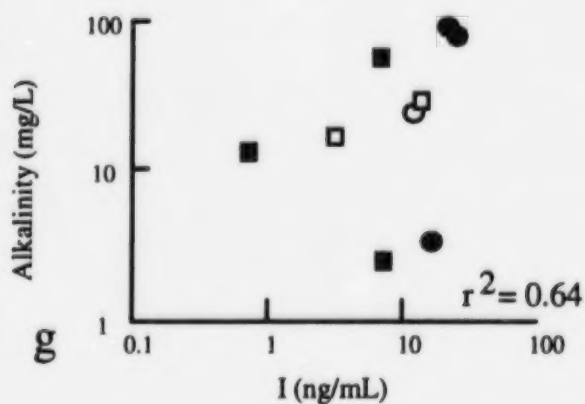
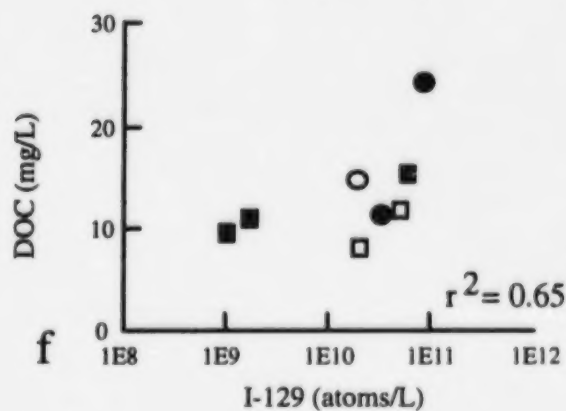
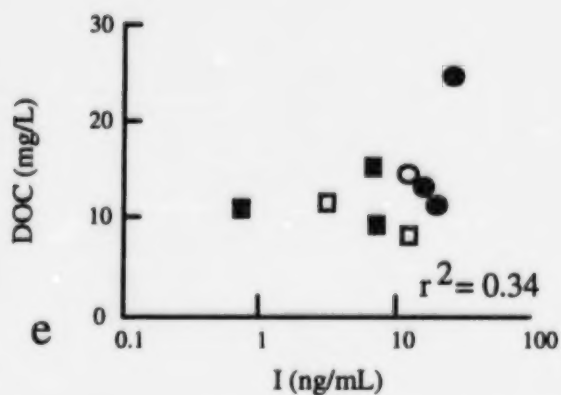
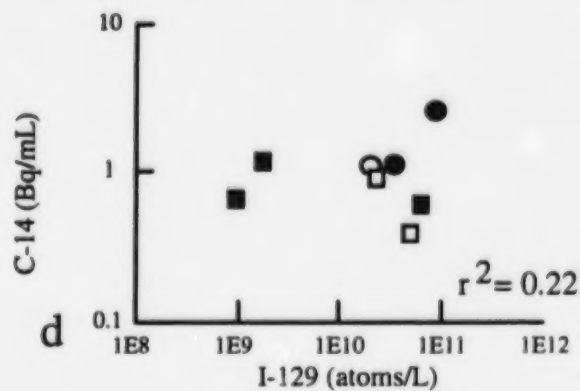
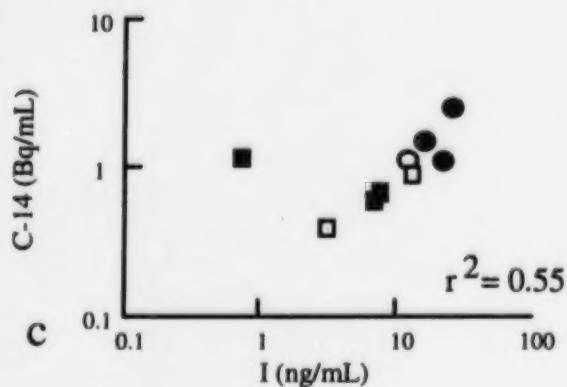
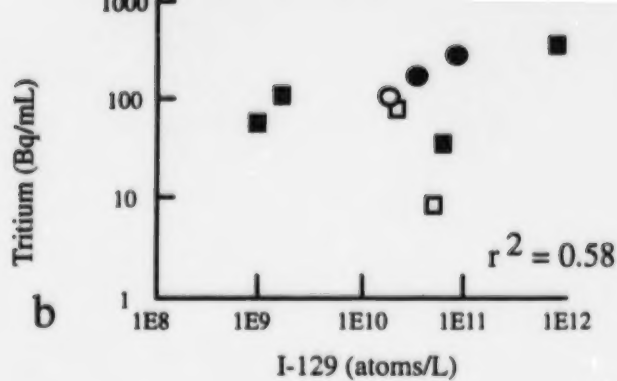
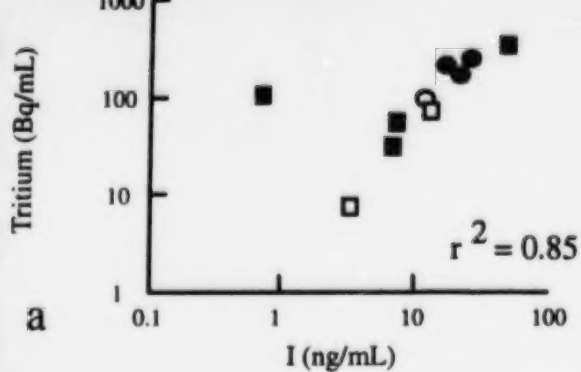


Figure 8: Correlation between I, ¹²⁹I, radio-nuclides and chemical species in contaminant plume waters

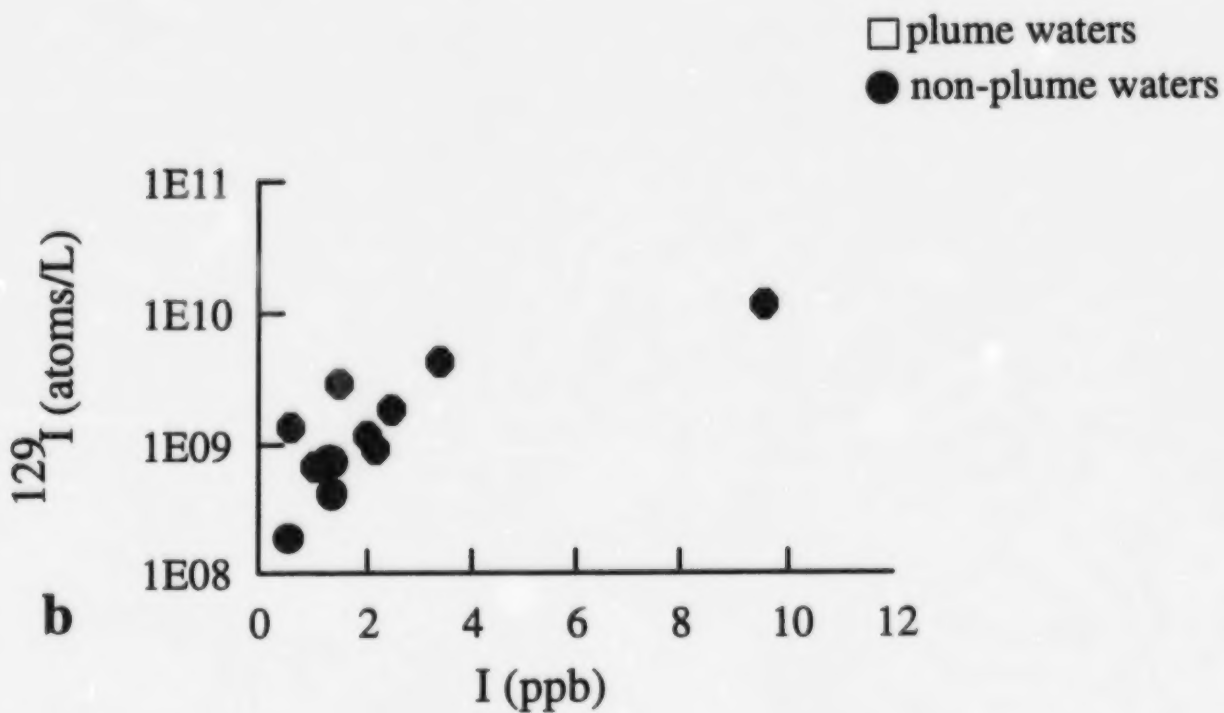
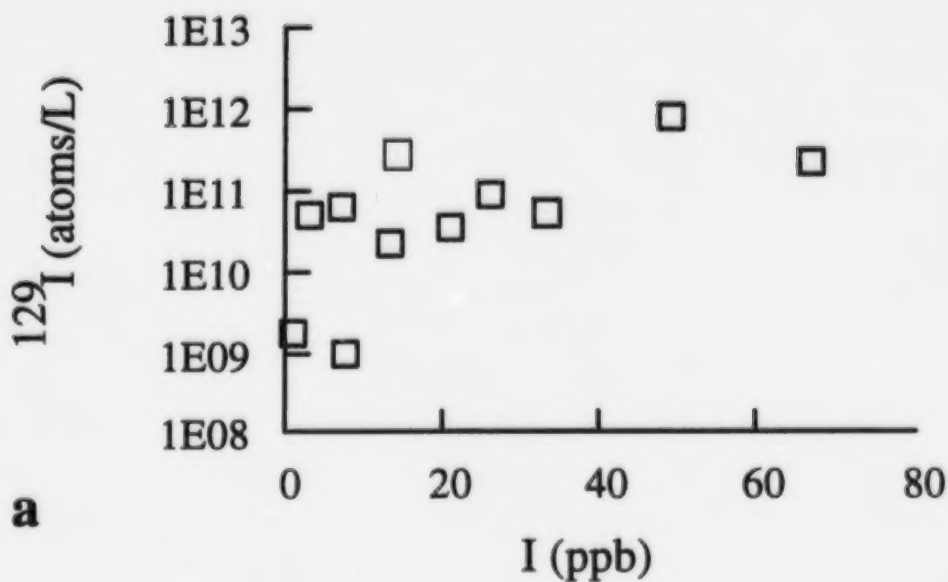


Figure 9: I-129 and I concentrations in groundwaters
a) within the contaminant plume and b) non-plume
waters.

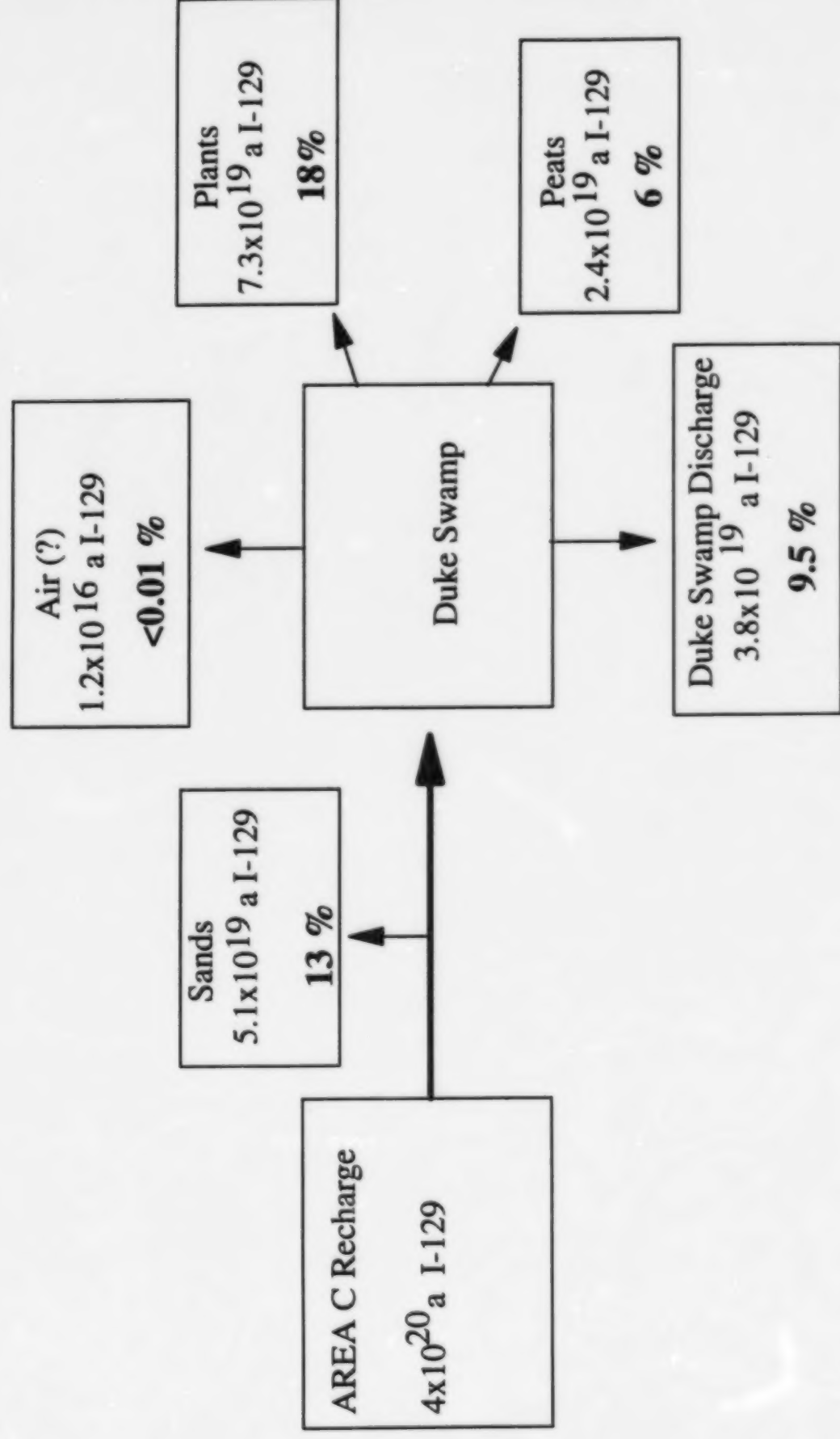


Figure 10: Empirical mass balance for I-129 at AREA C

Appendix

Annotated Bibliography

H. Beaujean, J. Bohenstingl, M. Laser, E. Merz & H. Schnez. *Environmental Behaviour of Radionuclides Released in the Nuclear Industry*, IAEA-SM-172/17, IAEA, Vienna, 1973.

GASEOUS RADIOACTIVE EMISSIONS FROM REPROCESSING PLANTS AND THEIR POSSIBLE REDUCTION

Describes ^3H , ^{85}Kr , ^{129}I and ^{131}I as the most important gaseous and volatile radioisotopes in reprocessing plants. Other than looking at other sources of Iodine information, did not find very useful, not really relevant for our study.

H. Behrens. *Environmental Migration of Long-Lived Radionuclides*. IAEA-SM-257/36, IAEA, Vienna, 1982.

NEW INSIGHTS INTO THE CHEMICAL BEHAVIOUR OF RADIOIODINE IN AQUATIC ENVIRONMENTS.

This study demonstrated that in surface fresh waters, iodide was to a large extent chemically converted by microbial action. The reactions involved extracellular enzymatic oxidation with subsequent incorporation of I into organic compounds (most likely proteins). It was found that iodate is reduced probably by biochemical reactions, which was more pronounced in soils than in surface waters. In surface fresh waters the formed organic radioiodine compounds were mainly in solution. In soils the radioiodine became bound to insoluble organic substances. The dissolved form of organic iodine was not precipitable as silver halide. Chemical and physico-chemical properties were described. Details on the iodine conversion influenced its fixation processes in the soil were given. Possible consequences of these reactions on the migration behaviour of radioiodine and on the performance as well as the interpretation of experiments in this context were discussed (Such as organic matter as well as density of microflora decrease with increasing depth or part of the dissolved organically bound iodine becomes bound to solid organic soil material by biogeochemical reaction).

H. Behrens. *Int. Conf. Nuclear and Radiochemistry*, pp.223-230, 1984.

SPECIATION OF RADIOIODINE IN AQUATIC AND TERRESTRIAL SYSTEMS UNDER THE INFLUENCE OF BIOGEOCHEMICAL PROCESSES.

In aerated surface and soil water, iodide underwent a chemical reaction which binds the iodine in dissolved organic compound (catalyzed by microbial activity, iodination of organics by extracellular enzymes). In soil/water systems iodine was bound on undissolved organics. It appeared that humic substances seem to play a considerable role in binding the converted iodine. Iodate was not formed under these oxidizing reactions, because it was found to be reduced thus involved in above process. The behaviour and fate of radionuclide in environment, basically is connected with the chemical state on one hand and with chemical conditions on the other.

P. Benes, E.T. Gjessing & E. Steinnes. *Water Research*, 10, pp.771-716. 1976.

INTERACTIONS BETWEEN HUMUS AND TRACE ELEMENTS IN FRESH WATER.

Interaction between humus and 18 elements in lake water was studied using centrifugation, ultracentrifugation and filtration through the ion exchange membranes. An association was found

between humus and trace elements; it depended on a concentration factor and pH. This association was low for halogens. No useful information about the relationship, between Iodine to humus in water, could be obtained by centrifugation or ion exchange due to no reproducible separation by the method used was achieved. Results of ultracentrifugation experiments illustrated that iodine and bromine was retained by the ultrafilter. This indicated that iodine is present not only as a simple halide ion (which should be retained either because of filtration effects or adsorption). Some kind of interaction cannot be excluded but no pronounced effect of concentration was found and retention may be due to other forms than associates with humus.

J. Bors. *Radiochimica Acta*. **51**, 1990

SORPTION OF RADIOIODINE IN ORGANO-CLAYS AND SOILS.

Treatment of bentonite, vermiculite, Cretaceous clay and horizons of chernozem soil with hexadecylpyridium (HDPY⁺) and benzethonium (BE⁺) exhibited sorption rates and amounts which are several order of magnitudes higher than those of the respective untreated samples.

J. Bors, H. Erten & R. Martens. *Radiochimica Acta*. **52/53**, pp. 317-325, 1991

SORPTION STUDIES OF RADIOIODINE ON SOILS WITH SPECIAL REFERENCES TO SOIL MICROBIAL BIOMASS.

Batch experiments with chernozem and podzol showed an initial rapid sorption of ¹²⁵I, followed by a long slow further increase. Incubation of soil samples under varied conditions delivered indications for the participation of soil microflora in iodine immobilization.

J. Bors & R. Martens. *Journal of Environmental Radioactivity*. **15**, pp.35-49, 1992.

THE CONTRIBUTION OF MICROBIAL BIOMASS TO THE ADSORPTION OF RADIOIODIDE IN SOILS.

The result of this investigation gave no clear evidence as to whether microbially mediated enzymatic processes or direct uptake by the cell mass is responsible for the influence of the biomass on adsorption. The experiment described involving different incubation temperatures gave some obvious indication that direct adsorption plays an important role. If enzymatic transformation processes were responsible, the increased metabolic activity at higher temperatures should cause increased adsorption. However, the opposite was observed and is explained by a reduced survival of microorganisms at prolonged higher incubation temperatures.

J. Bors, R. Martens & W. Kuhn. *Radiochimica Acta*. **44/45**, pp. 201-206, 1988.

STUDIES ON THE ROLE OF NATURAL AND ANTHROPOGENIC ORGANIC SUBSTANCES IN THE MOBILITY OF RADIOIODINE IN SOILS.

Experiments with ¹²⁵I revealed the general tendency of increasing distribution coefficients (K_d-values) with increasing organic C-content of different horizons in podzolic soil profile. These experiments were aimed at finding out if dibutylphosphate (DBP), nitriloacetic acid (NTA) and ethylenediaminetetraacetic acid (EDTA) can influence the sorption of Iodine.

F.P. Brauer & N.E. Ballou. . *Isotope Ratios as Pollutant Source and Behaviour Indicators*, IAEA-SM-191/20, IAEA, Vienna, 1975.

ISOTOPIC RATIOS AND OTHER RADIONUCLIDES AS NUCLEAR POWER POLLUTION INDICATORS.

Measurements of various radionuclides in environmental samples were carried out to test their application in the detection of nuclear plant effluents. The transfer pathways of atmospheric ^{129}I to food materials was studied by means of $^{129}\text{I}/^{127}\text{I}$ analysis of environmental samples. The absorption by vegetation of atmospheric iodine was found to be significant. The $^{129}\text{I}/^{127}\text{I}$ ratio was observed to decrease in the pathway from the atmosphere to food.

F.P. Brauer & R.S. Strebin, Jr. *Environmental Migration of Long-Lived Radionuclides*. IAEA-SM-257/43, IAEA, Vienna, 1982.

ENVIRONMENTAL CONCENTRATION AND MIGRATION OF ^{129}I

^{129}I was found to accumulate in the top soil and litter layer. The surface concentration of ^{129}I in the forest communities was found to be several times higher than that of nearby grass communities.

^{129}I is anionic and travels with water flow. Once the ^{129}I enters the hydrosphere it migrates with the water with little or no hold up by exchange with cationic exchange such as soil or silt. As ^{129}I is dispersed (some entering the food chain) it becomes isotopically diluted with natural ^{127}I . The retention of ^{129}I in mineral and ores indicate that under some conditions, very long time periods are required for migration in order that effective retention can be achieved. (Had a comparison of ^{129}I and ^{226}Ra in uranium mineral and ore samples.)

K.I. Burns & M.R. Ryan. *Journal of Radioanalytical and Nuclear Chemistry*. **194** (1), pp.15-23, 1995.

DETERMINATION OF ^{129}I LOW LEVEL RADIOACTIVE WASTE BY RADIOCHEMICAL INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS.

Article summarizes the method and results from analysis of two waste streams.

D.R. Champ, J.L. Young, D.E. Robertson & K.H. Abel. *Water Poll.Res. J. Canada*. **19** (2), 1984. Environmental Research Branch, Chalk River Nuclear Laboratories, Chalk River, Ontario K0J 1J0

CHEMICAL SPECIATION OF LONG-LIVED RADIONUCLIDES IN A SHALLOW GROUNDWATER FLOW SYSTEM.

The chemical speciation, in addition to ionic particulate forms of long-lived isotopes (iodine being one of them) was determined in four contaminant plumes in Chalk River. Anionic species were the predominant mobile form for many of the elements. Complexation by organic ligands, both natural and synthetic was postulated to be important in the mobilizing of the radionuclides. Iodine forms weakly organic complexes, so should exist as I^- in natural waters. The speciation is consistent with formation of anionic organic complexes (Behrens, 1980). Organic complexation could result in rapidly migrating iodine if soluble complexes are formed. However, retardation may result if the organic ligands also absorb to the soils (Davis & Leckie, 1978). The thermodynamic prediction of I^- solubilities would, in this case, result in maximal prediction of migration.

J.V. Christiansen & L. Carlsen. *Radiochimica Acta*. **52/53** part II, pp.327-333, 1991.

ENZYMATICALLY CONTROLLED IODINATION REACTIONS IN TERRESTRIAL ENVIRONMENT.

Humic acids are iodinated either by elemental iodine/hypoiodous acid or by iodide in the presence of enzymes of the peroxidase group and hydrogen peroxide. Possible influences of the experimental findings on the migration behaviour of radioiodide in the terrestrial environment are discussed.

G.R. Choppin. *Radiochimica Acta*. **44/45**, pp. 23-28, 1988.

HUMICS AND RADIONUCLIDE MIGRATION.

Interesting background information on description of humic complexation, colloid formation and their properties in migration of actinides.

B.L. Cohen. *Health Physics*. **49** (2), pp. 279-285, 1985.

THE ORIGIN OF I IN SOIL AND THE ^{129}I PROBLEM.

Here the authors hypothesized that the I in soil originated from the oceans, but recent data showed no correlation between concentration of I in soil and proximity to oceans. This argues strongly against oceanic origin theory. Some problems with long distance atmospheric transport were pointed out. It showed that the balance between I input to soil during soil formation by rock weathering, and output from soil by erosion left little room for contribution from oceanic sources. It concluded that only a small fraction of I in soil was of oceanic origin.

G.J. Evans, R.E. Jervis & E.G. Csillag. *Journal of Radioanalytical and Nuclear Chemistry*. **124** (1), pp. 145-155, 1988.

THE AIR/WATER PARTITIONING OF RADIOIODINE: AN EXPERIMENTAL ASSESSMENT.

Radiochemical methods of determining liquid and gas phase speciation, along with experimental results were presented with emphasis on the factors affecting the chemical speciation of iodine, such as pH, redox potential, total iodine concentration and intensity of radiation field.

G.J. Evans & K.A. Hammad. *Journal of Radioanalytical and Nuclear Chemistry*. **192** (2), pp. 239-247, 1995.

RADIOANALYTICAL STUDIES OF IODINE BEHAVIOUR IN THE ENVIRONMENT.

Radiochemical techniques were used to evaluate various aspects of behaviour of iodine in the environment. The natural iodine content of plant, water and soil samples from three sites were determined using preconcentration neutron activation analysis. Iodide was found to absorb more extensively than iodate, although for most of the solid/water systems examined, a substantial portion of the iodate was slowly reduced to iodide.

J. Fabryka-Martin, H. Bentley, D. Elmore & P.L. Airey. *Geochimica et Cosmochimica Acta*. **49**, pp.337-347, 1985.

NATURAL IODINE-129 AS AN ENVIRONMENTAL TRACER.

This article describes why ^{129}I could be used as an environmental tracer. The pre-bomb atmospheric ratios $^{129}\text{I}/\text{I}$ should have been constant through time and space and is the starting value in groundwater recharge. Subsequent ratio changes in ground water should be determined by isotope contribution from three sources: recharge waters, iodine leached from the formations and in situ uranium fission). Atmospheric equilibrium estimates for ^{129}I and pre-bomb atmospheric equilibrium are presented.

J. Fabryka-Martin and S.N. Davis. *Nuclear Instruments and Methods in Physics Research*. **B29**, pp. 361-371, 1987.

APPLICATIONS OF ^{129}I AND ^{36}Cl IN HYDROLOGY.

Additional information is presented on iodine and its use as an environmental tracer. Several sources of ^{129}I are described. Cosmic ray activation through neutron capture by Xe and Ar in upper atmosphere accounts for most of the atmospheric inventory of ^{129}I .

J.T. Fabryka-Martin, S.N. Davis, D. Elmore & P.W. Kubik. *Geochimica et Cosmochimica Acta*. **53**, pp.1817-1823, 1989.

IN SITU PRODUCTION AND MIGRATION OF ^{129}I IN STRIPA GRANITE, SWEDEN.
Atmospheric sources of ^{129}I , subsurface production of ^{129}I in stripa granite and prebomb water ratio for ^{129}I are discussed.

R. Fuge & C.C. Johnson. *Environmental Geochem. Hlth.* **8**, pp.31-54, 1986.

THE GEOCHEMISTRY OF IODINE-A REVIEW.

This paper describes the chemistry of iodine and its geochemical classification in naturally occurring minerals, in the lithosphere, soils, hydrosphere, atmosphere, biosphere and the geochemical cycle of iodine. It illustrates that IO_3^- is present in alkaline medium but in acidic environments the oxidation potential of $\text{I}_2\text{-IO}_3^-$ is very high and is unlikely to take place ($E_h\text{-pH}$ diagram of Iodine aqueous species).

M. Fukui, Y. Fujikawa & N. Satta. *Journal of Environmental Radioactivity*. **31** (2), pp. 199-216, 1996.

FACTORS AFFECTING INTERACTION OF RADIOIODIDE AND IODATE SPECIES WITH SOIL.

Results were obtained which showed that an increase in temperature in ambient air during drying or heating of samples during batch experiments of soil samples markedly decreased the K_d values. The grain size had an inverse relationship to K_d of IO_3^- where I^- K_d was independent of grain size. This observation indicated that the adsorption of IO_3^- is based on simple ion exchange, whereas for I^- is based on coupled sorption mechanism. Addition of CaCO_3 , Ca(OH)_2 , CaCl_2 or CaSO_4 did not suppress the uptake of I^- .

J. Handl. *Radiochimica Acta*. **72**, pp.33-38, 1996.

CONCENTRATIONS OF ^{129}I IN THE BIOSPHERE.

This study indicated that the worldwide distribution of the biospheric ^{129}I occurring in areas not affected by nuclear installations are result of the complete mixing of ^{129}I with natural iodine.

P.C. Ho. *Radiochimica Acta*. **51**, pp. 33-47, 1990.

A REVIEW OF THE ORGANIC GEOCHEMISTRY OF SHALES AND POSSIBLE INTERACTION

Shales have been suggested as host rocks for high level nuclear waste repositories. Studies have shown the interaction of nuclides with organic compounds found in shales. Organic compounds that have been identified from these shales are mainly hydrocarbons and carboxylates along with small amounts of other compounds.

M.V. Kantelo, B. Tiffany & T.J. Anderson. *Environmental Migration of Long-Lived Radionuclides*. IAEA-SM-257/53P, IAEA, Vienna, 1982.

IODINE-129 DISTRIBUTION IN THE TERRESTRIAL ENVIRONMENT

SURROUNDING A NUCLEAR FUEL REPROCESSING PLANT AFTER 25 YEARS OF OPERATION.

The distribution of ^{129}I in the terrestrial environment surrounding the given study area after 25 years of operation was determined. Information on analytical procedures was of interest based on previous work involving the combustion of the sample to separate iodine, neutron activation, purification by distillation and solvent extraction, measurement of activation products by γ -spectroscopy.

R.W.D. Killey, R.R. Rao & S. Eyvindson. *AECL 1135*, 1993. Atomic Energy of Canada Limited, Chalk River, Ontario K0J 1J0, Canada

RADIOCARBON SPECIATION AND DISTRIBUTION IN AN AQUIFER PLUME AND GROUNDWATER DISCHARGE AREA, CHALK RIVER ONTARIO.

This paper deals primarily with carbon isotopes in an aquifer plume and a groundwater discharge area (Duke Swamp). This article is of interest to our study because it describes the geology of our study area, uses piezometers for sampling which we are using, and gives us other available data to see if there are other correlations with the transportation of iodine in the groundwater system.

J.T. Koch, D.B. Rachar & B.D. Kay. *Canadian Journal of Soil Science*. **69**, pp. 127-135, 1989.

MICROBIAL PARTICIPATION IN IODIDE REMOVAL FROM SOLUTION BY ORGANIC SOILS.

The migration of ^{129}I in the biosphere may be changed if the nuclide passes through an organic soil. The reactivity and transportability may be altered in organic soils by processes in which microorganisms participate. The authors conclude (after experimenting with glucose, thymol and γ -radiation to either suppress or stimulate I^- removal) that microorganisms play an important role in I^- removal from solution in organic soils.

D.C. Kocher. *Environmental Migration of Long-Lived Radionuclides*. **IAEA-SM-257/56**, IAEA, Vienna, 1982.

ON THE LONG-TERM BEHAVIOUR OF IODINE-129 IN THE TERRESTRIAL ENVIRONMENT.

This paper was an analysis of available data on the dynamic global transport of naturally occurring stable iodine for the purpose of predicting the long-term, worldwide-average behaviour of ^{129}I in the terrestrial environment following releases to the atmosphere. Parts of the terrestrial environment considered in this study included the surface soil region, with an assumed depth of 1m, and the shallow and deep lithosphere in which ^{129}I is transported via groundwater flow. The mean residence time of ^{129}I in the surface soil region with respect to removal to ocean surface waters or the subsurface regions of lithosphere is predicted to be 4×10^3 yr. The predicted mean residence time for ^{129}I in surface soil concludes that foodstuffs were contaminated with ^{129}I via root uptake by plants. The predicted mean residence time for ^{129}I in shallow and deep subsurface compartments of the lithosphere are 1×10^3 yr. and 4×10^4 yr., respectively. The values were about a factor of five greater than the corresponding mean residence times for groundwater in these compartments. ^{129}I transport via groundwater flow was not greatly retarded and led to the conclusion that the subsurface lithosphere is not significant sink for isolating globally circulating ^{129}I from man.

W. Kuhn, J. Handl & H.P. Schätzler. *Environmental Behaviour of Radionuclides Released in the Nuclear Industry*, IAEA-SM-172/19, IAEA, Vienna, 1973.

TRANSPORT OF ^{131}I , ^{137}Cs , ^{106}Ru , ^{144}Ce AND ^{54}Mn IN AN UNDISTURBED SOIL UNDER NATURAL ENVIRONMENT CONDITIONS.

The penetration of radionuclides into the soil was determined by γ -spectroscopy and autoradiography. Contamination of the fission products, mainly cationic, were only found in the superficial soil layer. Ion exchange properties of natural soils were attributed mainly to clay fractions. Additional investigation showed that anions (like nitrate ions, iodides and ammoniacal complexes) are more mobile than cations. They penetrated more deeply into the soil within a shorter period than cations resulting in the detection at greater depths after short time.

H. Lang & C. Wolfrum. *Water-Rock Interaction*. pp. 417-420, 1989.

NUCLIDE SORPTION ON HETEROGENEOUS NATURAL SURFACES.

The sorption behaviour of different concentrations of radioactive Cs^+ , Sr^{2+} , and I^- in natural sediment-groundwater-systems was studied in the laboratory. It was found that the behaviour of ionic solutes in natural groundwater and sediment samples can be evaluated on the basis of exponential isotherms. The applicability of special isotherms onto the sorption data gave insight into the distribution of sorption sites available for specific radionuclides.

B.E. Lehmann & H.H. Loosli. *Water-Rock Interaction*. pp. 429-432, 1989.

SUBSURFACE PRODUCTION OF ^3He , ^4He , ^{36}Cl , ^{37}Ar , ^{39}Ar , ^{129}I AND ^{222}Rn IN THE CRYSTALLINE AND THE SEDIMENTS OF NORTHERN SWITZERLAND.

Production rates and equilibrium concentrations in closed volumes of rock were calculated for 37 locations for all the isotopes.

K.H. Leiser & TH. Steinkopff. *Radiochimica Acta*. **46**, pp. 49-55, 1989.

CHEMISTRY OF RADIOACTIVE IODINE IN THE HYDROSPHERE AND IN THE GEOSPHERE.

The chemistry of iodine in the hydrosphere and the sorption of radioactive iodine on sediments at low and high salt concentrations was discussed. Special attention was paid to the carboniferous particles in the sediments and their influence on sorption of iodine. The following conclusions were drawn; at low concentrations of iodine ($<10^{-6}$ mol/l) and if organic compounds of iodine were not taken into account, I^- was the dominant species of iodine in the range of pH and Eh generally encountered in groundwater. The sorption ratio of I^- on the inorganic components of sediments (the minerals) was very small. It depended on the specific surface area of the minerals and on the salinity. Carboniferous particles, organic substances, and microorganisms acted as iodine traps. They took up considerable amounts of iodine by very slow one directional processes resulting in sorption ratios of the order of 10^3 to 10^4 ml/g of carboniferous particles at low salinity and of the order of 10^2 to 10^3 mg/g at high salinity. The effectiveness of these traps for radioactive iodine depends on their content of reactive organic compounds and microorganisms, and on the specific activity of radioiodine.

C.W. Miller & F.O. Hoffman. *Environmental Migration of Long-Lived Radionuclides*. IAEA-SM-257/63, IAEA, Vienna, 1982.

AN ANALYSIS OF REPORTED VALUES OF THE ENVIRONMENTAL HALF-LIFE FOR RADIONUCLIDES DEPOSITED ON THE SURFACES OF VEGETATION.

Factors affecting the variability of the environmental half-time, T_w , were related to the physico-chemical form of the depositing substance, vegetation type & growth form, climate, season and experimental procedure. T_w values were generally lower for growing vegetation compared to the dormant vegetation. T_w values for iodine vapour and iodine particulates are less than values of T_w reported for particulates in other elements. Other background information is presented.

G.M. Milton, R.J. Cornett, S.J. Kramer & A. Vezina. *Radiochimica Acta*. **58/59**, pp. 291-296, 1992.

TRANSFER OF IODINE AND TECHNETIUM FROM SURFACE WATERS TO SEDIMENTS.

This work measured the partitioning and rates of transfer of ^{125}I , ^{131}I and ^{99}Tc from soluble phase to the particulate fraction and to surficial organic rich sediments. It was observed that all radioiodine introduced was found in the >500 MW fraction with 60% in the >10000 MW fraction. The behaviour was consistent with in situ behaviour previously observed and supported the hypothesis that iodine reaction with organics is a controlling process in natural waters. The rate of conversion is dependent on pH and size of organic molecule.

J.E. Moran, U. Fehn & J.S. Hanor. *Geochimica et Cosmochimica Acta*. **59** (24), pp. 5055-5069, 1995.

DETERMINATION OF SOURCE AGES AND MIGRATION PATTERNS OF BRINES FROM THE U.S. GULF COAST BASIN USING ^{129}I .

Use of ^{129}I gave a dimension, namely time, to isotopic studies of fluid movement in sedimentary basins in which large accumulation of organic materials are present. The cosmogenic ^{129}I component was used to date hydrologically isolated waters and, indirectly, associated hydrocarbons.

Y. Muramatsu & Y. Ohmomo. *The Science of Total Environment*. **48**, pp. 33-43, 1986.

IODINE-129 AND IODINE-127 IN ENVIRONMENTAL SAMPLES COLLECTED FROM TOKAIMURA/IBARAKI, JAPAN.

This article describes the neutron activation analysis for determination of ^{129}I and ^{127}I in soil, pine needles and algae samples in the vicinity of a nuclear fuel reprocessing plant. Sampling and analytical techniques were of interest.

Y. Muramatsu & Y. Ohmomo. *Journal of Radioanalytical and Nuclear Chemistry*. **124** (1), pp. 123-134, 1988.

TRACER EXPERIMENTS FOR THE DETERMINATION OF CHEMICAL FORMS OF RADIOIODINE IN WATER SAMPLES.

A variety of chemical species of iodine are known (I^- , IO^- , IO_3^- , IO_4^- , I_2 , organic forms, etc.) However, it was thought that the major chemical forms of iodine in aquatic environment were iodide (I^-) and iodate (IO_3^-). Hypoiodite (IO^-) was stable only in alkaline solutions. The behaviour of iodine in the environment depended on its chemical forms. The authors found it useful studying the species that exist in aquatic environments in order to predict the biological accumulation of artificial ^{129}I and ^{127}I in the environment. Two methods were used, isotope exchange and anion exchanger column, for the determination of chemical forms of radioiodine (iodide and iodate) in water samples. It was observed that iodide was converted to the iodate form in seawater and tap water samples.

Y. Muramatsu, S. Uchida, M. Sumiya, Y. Ohmomo & H. Obata. *Water, Air and Soil Pollution*. **45**, pp. 157-171, 1989.

TRACER EXPERIMENTS ON TRANSFER OF RADIO-IODINE IN THE SOIL-RICE PLANT SYSTEM.

Background information on ^{129}I is presented.

Y. Muramatsu, S. Uchida, P. Sriyotha & K. Sriyotha. *Water, Air and Soil Pollution*. **49**, pp. 125-138, 1990.

SOME CONSIDERATIONS OF THE SORPTION AND DESORPTION PHENOMENA OF IODIDE AND IODATE ON SOIL.

This paper shows that sorption of I⁻ by soils is greatly reduced by air drying and heating treatments.

Y. Muramatsu & S. Yoshida. *Journal of Radioanalytical and Nuclear Chemistry*. **169** (1), pp. 73-80, 1992.

NEUTRON ACTIVATION ANALYSIS OF IODINE IN SOIL.

The NAA method for analysis of iodine is described. Simple pre-irradiation procedures for the separation of iodine from the soil were developed. Soil is heated in a quartz tube and the evaporated iodine is collected in activated charcoal, which is then irradiated by neutrons and the ^{127}I produced is measured.

Y. Muramatsu & S. Yoshida. *Journal of Radioanalytical and Nuclear Chemistry*. **197** (1), pp. 149-159, 1995.

DETERMINATION OF ^{129}I AND ^{127}I IN ENVIRONMENTAL SAMPLES BY NEUTRON ACTIVATION ANALYSIS (NAA) AND INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS).

Analytical procedures were developed and applied to soil and water samples from various locations. Analytical speed of ^{129}I and ^{127}I analysis by ICP-MS was found to be high. Sensitivity limitations and detection limits of the methods were illustrated.

Y. Muramatsu & S. Yoshida. *Atmospheric Environment*. **29** (1), pp. 21-25, 1995.

VOLATILIZATION OF METHYL IODIDE FROM SOIL-PLANT SYSTEM.

Iodine was found to be volatilized from a soil-plant system into the atmosphere, in the form of CH_3I , methyl iodide. Iodine emissions were greater from potted plants than bare soil, and was especially noticeable from rice plants cultivated under flooding. Methyl iodide was presumed to have been synthesized by microbes in the soil under possible anaerobic conditions. The work improved the understanding of the biogeochemical cycle of iodine.

Y. Muramatsu, S. Yoshida & T. Ban-nai. *Journal of Radioanalytical and Nuclear Chemistry*. **194** (2), pp. 303-310, 1995.

TRACER EXPERIMENTS ON THE BEHAVIOUR OF RADIOIODINE IN THE SOIL-PLANT-ATMOSPHERE SYSTEM.

Further information is provided on previous research of this group (59).

NCRP REPORT No. 75. 1983. National Council on Radiation Protection and Measurements, 7910 Woodmount Avenue, Bethesda, MD, 20814

IODINE-129: EVALUATION OF RELEASE FROM NUCLEAR POWER GENERATION

This paper describes geographical sources and the distribution of stable iodine and ^{129}I ; releases of anthropogenic ^{129}I to the environment; human thyroid ^{129}I exposures from dietary sources; limits to the biological significance of ^{129}I and control measures. Very good background information on ^{129}I .

M.H. Noack. M. Sc. Thesis, Trent University. 1994

ESTIMATING GROUNDWATER VELOCITY FOR SHALLOW UNCONFINED AQUIFER USING TH $^3\text{H}/^4\text{He}$ DATING TECHNIQUE: A COMPARISON TO OTHER HYDROGEOLOGIC METHODS.

The hydrogeology of the proposed IRUS site (study area C) was of interest.

J. Paquette, D.J. Wren & B.L. Ford. *American Chemical Society Symposium Series The Three Mile Island Accident : Diagnosis and Prognosis.* 293, pp. 193-210, 1986.

IODINE CHEMISTRY.

This paper describes the chemistry of iodine in aqueous solution, including thermodynamic and kinetic calculations of various aqueous iodine reactions (of interest to our study are interactions with organic materials) that contributed to the low concentration of radioactive iodine observed in gas phase following the three mile island-2 nuclear reactor accident.

P.J. Parsons. *AECL 1038*, 1960. Atomic Energy of Canada Limited, Chalk River, Ontario K0J 1J0, Canada.

MOVEMENT OF RADIOACTIVE WASTE THROUGH SOIL:

Soil and Ground-Water Investigation in Lower Perch Lake Basin CRER-932

An investigation of soil and groundwater was made in Perch Lake Swamp where fission products are moving through the soil from the waste disposal area 'A' towards Perch Lake. Useful background information is provided that is relevant to objectives for our study (such as methods used in soil testing).

M.E. Raja & K.L. Babcock. *Soil Science* 91 (1), 1961. University of California, Berkeley

SOIL CHEMISTRY OF RADIO-IODINE

The behaviour of carrier-free ^{131}I in two Californian soils, in two clay minerals, and in peat was studied. The results of pretreatment (by autoclaving, oxidation with peroxide and digestion with alcohol, as well as extraction of ^{131}I with various salt solutions) all indicate that the large fraction of ^{131}I retained by soils is due to the reaction with organic matter. This paper provides useful background information on methods used in I analysis of soil samples.

D.E. Robertson & R.W. Perkins. *Isotope Ratios as Pollutant Source and Behaviour Indicators*, IAEA-SM-191/24, IAEA, Vienna, 1975.

RADIOISOTOPES RATIOS IN CHARACTERIZING THE MOVEMENT OF DIFFERENT PHYSICAL AND CHEMICAL SPECIES THROUGH NATURAL SOILS.

Radioisotopes ratios were used in characterizing the movement of different physical and chemical species through natural soils. The mobility of radionuclides in effluent water during movement through the soil is greatly dependent upon the physicochemical forms of the radionuclides.

Radionuclides in particulate and cationic forms are nearly quantitatively retained in the soil by sorption unto metal phases. Radionuclides in anionic and soluble nonionic forms are relatively mobile and are retained by the soil to a much lesser degree. The study looked at $^{131}\text{I}/^{133}\text{I}$ and observed that it was present in anionic form. The anionic form is more soluble than the cationic forms. It is present mainly as a negative ion in spring water and was not retained in the soil of the study site. This study raised the question of iodine being transported with minimal uptake and retention by the aquatic biosphere and sedimentary mineral phases. To answer this question it is necessary to study biogeochemical behaviour of this radionuclide in natural water ecosystems or the laboratory.

A. Saas & A. Crauby. *Environmental Behaviour of Radionuclides Released in the Nuclear Industry*, IAEA-SM-172/57, IAEA, Vienna, 1973.

MECANISMES DE TRANSFER DANS LES SOLS CULTIVES DES RADIONUCLEIDES REJETES PAR LES CENTRALES ELECTRO-NUCLEAIRES DANS LE SYSTEM FLEUVE-SOL IRRIGUE-NAPPE

This paper studied the effects of the quality of river water, irrigation channel water and groundwater on radionuclide mobility in cultivated soils. The study described relates to a number of radionuclides including ^{131}I . Knowledge of the transfer mechanisms permitted an evaluation of the risk of the contamination of the food chain and groundwater. The study also demonstrated new aspects of the behaviour of radionuclides as a function of organomineral pollution, by industrial and domestic waste of water, into which they are discharged. This pollution has a considerable effect on radionuclide profile in the soil. The water-soluble complexes persist in the soil and migrate downwards towards the water table if they are not biodegradable or are slightly so. The stability of these complexes is a function of the pH of the soil and its physico-chemical characteristic.

D.R. Schink, P.H. Santschi, O. Corapcioglu, P. Sharma & U. Fehn. *Earth and Planetary Science Letters*. **135**, pp. 131-138, 1995.

^{129}I IN GULF OF MEXICO WATERS.

The build up of new ^{129}I is readily detectable in the upper waters of the Gulf of Mexico. ^{129}I offers a non-steady-state water mass tracer with an input function distinctly different from the CFCs, ^{14}C or ^3H . It offers a new and different perspective on water mass movements.

K. Schmitz & D.C. Aumann. *Journal of Radioanalytical and Nuclear Chemistry*. **198** (1), pp.229-236, 1995.

A STUDY OF THE ASSOCIATION OF TWO IODINE ISOTOPES OF NATURAL ^{127}I AND OF THE FISSION PRODUCT ^{129}I , WITH SOIL COMPONENTS USING SEQUENTIAL EXTRACTION PROCEDURE.

From this study it is evident that ^{129}I much more mobile in aqueous solution and hence more available for plant-root uptake than ^{127}I , which is bound or effectively sorbed to components of the soil. Other forms of iodine which were determined for both isotopes were exchangeable iodine, iodine bound to metal oxides and iodine bound to organic matter.

H. Schüttelkopff & M. Pimpl. *Environmental Migration of Long-Lived Radionuclides*. IAEA-SM-257/100, IAEA, Vienna, 1982.

RADIOECOLOGICAL STUDIES ON PLUTONIUM AND IODINE-129 IN THE

SURROUNDINGS OF THE KARLSRUHE REPROCESSING PLANT.

The ^{129}I contamination of environmental air, soil and milk was measured. Soil contamination was studied very thoroughly. ^{129}I is transported into lower soil layers at very slow rates, if at all.

M.I. Sheppard, D.H. Thibault & J.H. Mitchell. *J. Environ. Qual.*, **16** (3), pp.273-284, 1987.

ELEMENT LEACHING AND CAPILLARY RISE IN SANDY SOIL CORES: EXPERIMENTAL RESULTS.

Leachate analysis and exhumation data for leachate of soil cores indicate that element mobility was $\text{Tc} \geq \text{I} > \text{Mo} \geq \text{Cr} > \text{U} \geq \text{Np}$, Cs, Th, with Tc being the most mobile and Th being the least. The analytical techniques were of interest in the leaching of sandy soil cores.

M.I. Sheppard, D.H. Thibault & P.A. Smith. *Applied Geochemistry*, **4**, pp. 423-432, 1989.

IODINE DISPERSION AND EFFECTS ON GROUNDWATER CHEMISTRY FOLLOWING A RELEASE TO A PEAT BOG, MANITOBA, CANADA.

This study investigated the migration and behaviour of I in sphagnum bog by releasing a 6M solution of KI to stimulate a pulse discharge of contaminated groundwater from a fracture in granitic rock.

M.I. Sheppard & D.H. Thibault. *Journal of Environmental Quality*, **20**, pp. 101-114, 1991.

A FOUR-YEAR MOBILITY STUDY OF SELECTED TRACE ELEMENTS AND HEAVY METALS.

Analysis of the soil/liquid partition coefficient indicated that the retention of these elements is primarily related to soil organic matter content and is dependent on pore water concentration.

M.I. Sheppard & D.H. Thibault. *Applied Geochemistry*, **4**, pp. 265-273, 1992.

CHEMICAL BEHAVIOUR OF IODINE IN ORGANIC AND MINERAL SOILS.

This study shows that the I present or added to surface soils will predominantly exist as soluble species and the amount of organic matter and the presence of Fe and Al oxides can be used to predict its retention. Iodine retention is primarily through physical association with the surface and the intricate structure of the organic matter, mass flow and diffusion. They play major roles in transporting I to soil micropores and structural cavities where it is temporarily confined. The loss of I^- is a 1st order reaction, indicating that this is merely the rate at which the water and dissolved I are absorbed into the inner structure of peat fabric. If the peat fabric contains very dry hydrophobic internal surfaces, then the I dissolved in pore water will only reach these inner spaces very slowly through diffusion. However, if peat is moist (saturated) Iodine may move more readily to these spaces. Iodine may be drawn to soil surfaces through weak electrostatic attraction.

M.I. Sheppard, D.H. Thibault, J. McMurry & P.A. Smith. *Water, Air and Soil Pollution*, **83**, pp. 51-67, 1995.

FACTORS AFFECTING THE SOIL SORPTION OF IODINE.

This shows that chlorine concentration plays an important role in iodine sorption in both mineral and organic soils. The presence of Cl decreased the loss of I^- from solution from 30 to 50% for organic and carbonated sandy soil respectively. The remaining I in solution was associated primarily with dissolved organic carbon (DOC). Iodide introduced to natural bog groundwater at 3 concentrations (10^{-3} , 10^{-1} , and 10 mg/l) remained as I^- and was not lost from solutions quickly

indicating that association with DOC is slow and does not depend on the DOC or iodine concentration.

M.I. Sheppard & J.L. Hawkins. *Journal of Environmental Radioactivity*. **29** (2), pp. 91-109, 1995.

IODINE AND MICROBIAL INTERACTIONS IN AN ORGANIC SOIL.

The results of this article suggest that microbes play only a minor and indirect role on iodine sorption through the decomposition of organic matter.

S.C. Sheppard. *AECL 11669*, 1996. Atomic Energy of Canada Limited, Pinawa, Manitoba R0E 1L0, Canada.

IMPORTANCE OF CHEMICAL SPECIATION OF IODINE IN RELATION TO DOSE ESTIMATES FROM ^{129}I .

Background information on ^{129}I is provided.

S.C. Sheppard & W.G. Evenden. *Journal of Environmental Radioactivity*. **7**, pp. 221-247, 1988.

THE ASSUMPTION OF LINEARITY IN SOIL AND PLANT CONCENTRATION RATIOS: AN EXPERIMENTAL EVALUATION.

The authors evaluated the use of concentrations ratios to describe the transfer of elements in the environment, since these ratios implies a linear relationship between the concentrations. The elements chosen were environmentally important elements, iodine being one of them. The result indicated that the relationship of leaf and leachate concentrations were not consistently linearly related to the total soil for each elements. Modeling difficulties implied by these concentration dependencies can be partially offset by including in the models the strong negative correlation between concentration ratio (CR) and partition coefficient (K_d).

S.C. Sheppard, W.G. Evenden & B.D. Amiro. *Journal of Environmental Radioactivity*. **21**, pp. 9-32, 1993.

INVESTIGATION OF SOIL-TO-PLANT PATHWAY FOR I, Br, Cl AND F.

The study investigated the behaviour of stable I, Br, Cl and F in a replicated, garden like plot experiment. Several lysimeter studies were integrated and sorption of halides on the soil decreased in order $\text{F} > \text{I} > \text{Br} > \text{Cl}$ and the sorption of I and F increased with time for at least 20 days.

S. Uchida, Y. Muramatsu, M. Sumiya & Y. Ohmomo. *Health Physics*. **60** (5), pp. 678-679, 1991.

BIOLOGICAL HALF-LIFE OF GASEOUS ELEMENTAL IODINE DEPOSITED ONTO RICE GRAINS.

This study determined the of biological half-life (T_b) of iodine deposited on rough rice grains, rice plants of four different growing stages exposed to elemental gaseous iodine.

S. Uchida, M. Sumiya, Y. Muramatsu, Y. Ohmomo, S. Yamaguchi, H. Obata, & M. Umebayashi. *Health Physics*. **55** (5), pp. 779-782, 1988.

DEPOSITION VELOCITY OF GASEOUS I TO RICE GRAINS.

This study used deposition velocity (V_g) as a parameter for estimating the I concentration in crops. It is applicable to pasture grass which covers the ground almost completely, but is not applicable to our study.

S. Yoshida Y. & Muramatsu. *Journal of Radioanalytical and Nuclear Chemistry*. 196 (2), pp.295-302, 1995.

DETERMINATION OF ORGANIC, INORGANIC AND PARTICULATE IODINE IN THE COASTAL ATMOSPHERE OF JAPAN.

A reliable method for sampling and analysis of atmospheric iodine species was developed.

D.C. Whitehead. *J.Sci.Fd Agric.* 25, pg.73-79, 1974.

The Sorption of Iodine by Soil Components.

The sorption of iodide by several surface soil component materials was examined over a range of pH. Organic matter sorbed iodide over a wide range of pH but ferric and aluminum oxides exhibited sorption of iodide only under acidic conditions. The sorption of iodide by surface soils at near neutral pH is due largely to the organic matter. The capacity of organic matter to sorb iodide apparently tends to increase as decomposition proceeds. At pH of 6.7 the sorption of I was closely related to the organic matter content. At pH <5.5 ferric and aluminum oxides as well as organic matter contributed significantly to the sorption of iodide by soils. Clay minerals sorb trace amounts of iodide. In alkaline soils, iodide is not readily available for plant uptake and that liming decreases the uptake of iodine by plants. The organic content was measured by dichromate oxidation.

D.C. Whitehead. *The journal of Soil Science* 29, pp.88-94, 1978.

IODINE IN SOIL PROFILES IN RELATION TO IRON AND ALUMINUM OXIDES AND ORGANIC MATTER.

Eighteen soil profiles from England and Wales were analysed for I and correlated with the content of free Al and Fe oxides and organic matter. The pattern of change in iodine content with depth varied considerably between the 18 sites. Iodine content was closely correlated with oxalate soluble Al $r=0.824$ but not with Fe $r=0.35$ or organic matter $r=0.37$. At a pH < 4.8, there is a better correlation with Fe than Al.

D.C. Whitehead. *Environment International*. 10, pp.321-339, 1984

THE DISTRIBUTION AND TRANSFORMATIONS OF IODINE IN THE ENVIRONMENT.

Atmospheric iodine was the major source of iodine in the soils and the process of enrichment continued throughout soil formation and development until ultimately an equilibrium concentration was attained. The retention of iodine in soils was due mainly to the organic matter and hydrous oxides of iron and aluminum. In humid areas, only small proportions of the total soil iodine was soluble in water or available for uptake by plants. The atmosphere was also a direct source of iodine in plants, and in some situations may be more important than the soil. Iodine may be lost from soils by leaching, volatilization and removal in crops, but the magnitude of these processes was difficult to assess. Most soils tended to retain iodine against leaching, and both inorganic and organic components appeared to be involved. The colloidal fraction of soils (clay and humified organic matter) carried a net negative charge and in general tended to repel anions. Nevertheless, sorption of the anions in soils did occur, particularly under acidic conditions, some of the sorption being non-specific and some specific to particular anions. This non-specific sorption occurs at the localized positive charges that occur on free hydrous oxides of iron and aluminum, and at the edges of the aluminosilicate clay mineral lattices where oxygen atoms are

not fully coordinated by aluminum or silicon atoms. These positive charges, which increase with decreasing pH, attract anions electrostatically, and the anions are readily exchangeable with those in the soil solution. Elemental iodine reportedly reacts spontaneously with thiol groups (Jirousek & Pritchard, 1971) and with polyphenols (Fawcett & Pritchard, 1971). Both thiols and polyphenols are present in soil organic matter so these reactions may occur in soils. In soils ferric oxide is likely to undergo continuous reprecipitation as a result of oxidation reduction reactions with organic matter thus increasing its capacity for sorption (Neal & Truesdale, 1976; Sugawara, 1958).